

# **Thermodynamics of Certain Refractory Compounds**

**DISCUSSION OF THEORETICAL STUDIES**

## List of Contributors

**ANTHROP, D. F., PH.D.,** Aerojet-General Nucleonics, San Ramon, California

**BARRIAULT, R. J., PH.D.,** (Deceased)

**DREIKORN, R. E., PH.D.,** IBM Components Div., Owego, N. Y.

**FEBER, R. C., PH.D.,** Los Alamos Scientific Lab., Los Alamos, New Mexico

**GRIFFEL, M., PH.D.,** Institute for Defense Analyses, Washington, D. C.

**LEIGH, C. H., PH.D.,** Parametrics Inc., Waltham, Mass.

**PANISH, M. B., PH.D.,** Bell Telephone Laboratories, Murray Hill, New Jersey

**SCHICK, H. L., PH.D.,** Lockheed Missiles & Space Co., Research Laboratories, Palo Alto, California

**WARD, C. H., PH.D.,** Auburn University, Auburn, Alabama



# Thermodynamics of Certain Refractory Compounds

HAROLD L. SCHICK

PRINCIPAL CONTRIBUTOR AND EDITOR  
IN COLLABORATION WITH THE CONTRIBUTORS

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## PREFACE

Since 1954, the Thermal & Solid State Branch of the Air Force Materials Laboratory has had a continuing interest in delineating materials-environment interactions under extreme thermal environments. This interest has most frequently resulted in the Air Force sponsorship of research programs aimed at the measurement of certain optical, thermophysical and thermodynamic properties of materials, kinetic studies of materials-environment interactions, the development of improved techniques for making these measurements, and the consolidation of literature data in some of these areas. This compilation spawned from these interests.

The magnitude of this effort, as has probably been the case with most works of this type, was underestimated. The work presented here is thus a contribution rather than a completed effort. It is hoped that others will continue in this effort. Thermodynamics has demonstrated itself as an important theoretical tool for predicting the chemical and physical behavior of materials under diverse environmental conditions. Much basic thermodynamic data have been and are now being obtained from many research programs throughout the world. However there has always been a distinct need for a program staffed by highly specialized personnel to evaluate, integrate, extrapolate and otherwise reduce these data to make them available in an interconsistent form directly useful to scientists and engineers for design purposes. The recent establishment of the National Standard Reference Data Program finally indicates the realization that we can no longer afford to be without such a continuing effort to help support and guide our research.

There are certain unique features to this work which have not generally been characteristic of other works of this type or at least not in this degree of detail or in this combination. It is believed that these are desirable features and should be considered in any future work of this type. The user's right to disagree has been profusely aided and abetted since the details of the critical analysis leading to the choice of accepted values are presented. Accuracy estimates are listed for most of the tabulated values. The fact that many of the tables extend to 6000°K and contain tabulation of data at close intervals of temperature is considered a great advantage. The program served as a proving ground for many computer techniques whose impact in the information generation, storage, and retrieval areas are yet to be felt.

The help of Mr. Edmund J. Rolinski and Dr. Emile Rutner of the Thermal & Solid State Branch is gratefully acknowledged as are the unknown visionaries in the higher echelons of the Department of Defense who assigned the special funds for the initiation of this effort. The thanks of the Air Force, the U. S. Government and the scientific community are due to the collaborators and contributors to this compilation. Special gratitude is due to Messrs Hyman Marcus, Jules I. Wittebort and Leo F. Salzberg whose vision, faith, cooperation, patience and understanding were essential in carrying this work to this point.

Paul W. Dimiduk  
Thermal and Solid State Branch  
Materials Physics Division  
Air Force Materials Laboratory



## FOREWORD

This publication is based on a final report (ASD-TR-61-260 Pt. II, 1964) prepared by the Research and Advanced Development Division of the Avco Corporation on Contract AF33(657)-8223 under Project No. 7360, The Chemistry and Physics of Materials: Task No. 736001, Thermodynamics and Heat Transfer. The work was administered under the direction of the Materials Physics Division of the Air Force Materials Laboratory, Research and Technology Division; the RTD monitor on the program was Mr. Paul Dimiduk of the Thermophysics Section. The data reported herein was compiled between 1 June 1962 and 31 December 1963. This work includes a study of the thermodynamics of the borides, carbides, nitrides, and oxides of 31 elements in the temperature range from 0° to 6000°K. The elements are (a) group II A -- beryllium, magnesium, calcium, and strontium; (b) group III B -- scandium, yttrium, and lanthanum, (c) group IV A -- silicon; (d) group IV B -- titanium, zirconium, and hafnium, (e) group V B -- vanadium, niobium, and tantalum; (f) group VI B -- chromium, molybdenum, and tungsten; (g) group VII B -- manganese, technetium, and rhenium; (h) group VIII -- rhodium, osmium, iridium, and platinum; (i) rare earths -- cerium, neodymium, samarium, gadolinium, and dysprosium; and (j) actinides -- uranium and thorium. More than 160 thermodynamic tables, together with comprehensive discussions, have been prepared. The work has been summarized in two volumes.

Volume 1, presents a summary of the techniques used to analyze thermodynamic data and gives the data analyses for refractories considered. Volume 2, is a compilation of thermodynamic tables generated on this project. It also contains a bibliography and subject index.

This work has been the result of the efforts of a group of scientists, including Doctors H. L. Schick, D. F. Anthrop, R. J. Barriault, R. E. Dreikorn, R. C. Feber, M. Griffel, C. H. Leigh, M. B. Faush, and C. L. Ward. Project Directors were R. J. Barriault (deceased June 1962), C. H. Leigh (June to December 1962), and H. L. Schick (December 1962 to December 1963). The contributions of different scientists can be identified by reference to the thermodynamic tables of Volume 2. Each of these tables is labeled with the initials of the responsible scientist and the approximate date of the analysis. The corresponding discussion in Volume 1 was also prepared by the same scientist.

His fellow co-workers wish to express their feeling of loss at the untimely passing of Dr. Roland J. Barriault at the beginning of this project in June, 1962. His enthusiasm and leadership were invaluable in a previous contract, AF 33 (616)-7327.

Prof. W. L. Klemperer of Harvard University has acted as consultant on spectroscopic and thermodynamic problems.

Many individuals located throughout the world have been kind enough to provide information to assist this work. An effort has been made to acknowledge such help below. Any omissions are entirely accidental.

L. Akerlind  
C. B. Alcock

University of Stockholm  
Imperial College of London

B. Aronsson	University of Uppsala
R. F. Barrow	Oxford University
C. Beckett	National Bureau of Standards
J. Berkowitz	Argonne National Laboratories
J. Berkowitz-Mattuck	Arthur D. Little Company
G. Brauer	University of Freiburg
L. Brewer	University of California
E. R. Cohen	North American Aviation
R. H. Crist	Union Carbide Research Institute
T. Dergazarian	Dow Chemical Company
P. Dimiduk	Research and Technology Division
R. T. Dolloff	National Carbon Company
T. B. Douglas	Heat Division, National Bureau of Standards, Washington, D. C.
J. W. M. DuMond	California Institute of Technology
J. Elliott	Massachusetts Institute of Technology
R. D. Freeman	Oklahoma State University
R. R. Freeman	Chemical Abstracts
M. A. Greenbaum	Rocket Power, Pasadena, California
E. Greenberg	Argonne National Laboratories
C. B. Henderson	Atlantic Research Corporation
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M. Hoch	University of Cincinnati
R. Honig	Radio Corporation of America
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R. Hultgren	University of California
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2. An NRC-OCT conference on critical tables of thermodynamic data held at the National Academy of Science on 14-15 March 1963 under the dual chairmanship of Prof. E. Westrum and Dr. G. Waddington.
3. The Stanford Research Institute Symposium on High Temperature Technology at Asilomar, California, in September 1963.
4. A JANAF Thermochemical Panel Meeting in New York City on 5-7 November 1963.

The cooperation of the library staffs at the Massachusetts Institute of Technology, the Cambridge Research Laboratories at Hanscom Field, The New York office of the Atomic Energy Commission, the Division of Technical Information Extension at Oak Ridge, and Avco RAD has been invaluable.

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One of us (H. L. Schick) would also like to express appreciation to Mr. R. Capraux of Lockheed Missiles and Space Company for support in the final stages of publishing this document.



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## INTRODUCTION TO GLOSSARY

a work of this scope, it is desirable to maintain a high degree of uniformity regard to symbols, abbreviations, and units. However, several problems preclude attainment of this high objective.

First of all, there are many cases where it is necessary to reproduce exactly the original author's symbols and units. Both the symbols and units may, of course, differ from those used by other workers in the field, or from those generally used throughout this present work.

Second, because of the limited number of letters in the Latin and Greek alphabets, and because of already well established symbols in different fields, there are bound to be certain symbols which must be used repeatedly for completely different quantities.

To overcome these difficulties, as complete a glossary as possible has been compiled herein. Further, to aid the casual user of this work, a page reference has been included so that he can refer to a typical usage of a particular symbol.

In volume 2, which contains the thermodynamic tables, it is believed that the highest degree of consistency of symbols and units has been attained since that volume is concerned with the "final output" product of the project. On the other hand, in volume 1 where the original "input data" are discussed, some variation may occur. However, by using the glossary, it is believed that there should be little difficulty in following the presentation.

In preparing the glossary, the symbols commonly used in crystallography and spectroscopy have been followed. Thus, in crystallography, symbols such as  $P_1$ ,  $A_2$ , etc., have been used to designate the crystal structure types. These types identify a material as to crystal system, space group, and number of atoms per unit cell. A complete listing of these types may be found elsewhere; e.g., Hansen, M. and K. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York (1958), Table C, p. 1270-1275. The present glossary gives only a cursory definition of these crystallographic symbols. Reference should be made to the cited work for a complete definition.

In spectroscopy, notations have been followed which agree with those in general use. For atomic species, the works by Charlotte Moore [Atomic Energy Levels, Natl. Bur. Stds. (U.S.), Circ. 467, vol. 1 (1949); vol. 2 (1952); and vol. 3 (1958)] represent a standard system. For diatomic molecules, one source is widely accepted; i.e., Herzberg, G., Molecular Spectra and Molecular Structures, I. Spectra of Diatomic Molecules, 2nd ed., Van Nostrand, New York (1950).

## INTRODUCTION TO GLOSSARY

With a term such as  $\Delta H$ , it may be noted that several subscripts and superscripts are possible. A superzero; i. e.,  $\Delta H^{\circ}$ , indicates a heat of reaction when materials are in their standard state (pure substances at 1 atm). A subscript such as an "f"; i. e.,  $\Delta H_f^{\circ}$ , indicates the heat of formation of a compound from the component elements in their standard states. Also, subscripts may be added to the above to identify the compound and the temperature. Thus,  $\Delta H_f^{\circ}, \text{TiO}_2, 298.15$  indicates the standard heat of formation of  $\text{TiO}_2$  from its component elements at  $298.15^{\circ}\text{K}$ . For convenience,  $298.15^{\circ}\text{K}$  is often rounded off to  $298^{\circ}\text{K}$  even though the figure  $298.15^{\circ}\text{K}$  is understood.

It is expected that this glossary will satisfy the requirements of the user regardless of whether he is referring to volume 1 or 2. However, the careful user will consult both volumes to understand this study fully.

# GLOSSARY OF SYMBOLS AND ABBREVIATIONS

## Latin Symbols

### A

Symbol	Page (where first found usually)	Explanation
a	1-57	Parameter defined on pages 1-57 and 1-58; not used elsewhere in this work
a	1-67	Symbol to define an electronic state of a diatomic molecule; e.g., $a^1\Delta$
a	1-157	Lattice parameter, usually in Å (i.e., $10^{-8}$ cm)
a	1-325	Thermodynamic activity
A	1-56	First term in equation $C_p = A + BT + \dots$
A	: 266	Coupling constant for diatomic molecules
Å	1-40	Angstroms = $10^{-8}$ cm
ACR	1-18	Abstracts of Classified Reports
AEC	1-18	Atomic Energy Commission
ANL	1-536	Argonne National Laboratory
ARPA	1-15	Advanced Research Projects Agency
ASD		Aeronautical Systems Division
ASM	1-10	American Society for Metals
A1	1-122	Crystal structure notation: face - centered cubic
A2	1-127	Crystal structure notation: body - centered cubic
A3	1-140	Crystal structure notation: hexagonal close-packed



A (Concl'd)

Symbol	Page	Explanation
A4	1-157	Crystal structure notation: cubic; i. e. , diamond-type
A13	1-127	Crystal structure notation: primitive cubic

B

b	1-58	Constant used in section IIIB1
b	1-67	Used to designate electronic state of a molecule; e.g. , $b^1\pi$
b	1-179	Lattice parameter
B	1-3	Boron
B	1-56	Second term in equation $C_p = A + BT + \dots$
$B_e$	1-39	Rotational constant for equilibrium separation of atoms
$B_v$	1-78	Rotational constant in vibrational state v
Be	1-3	Beryllium
BETA	1-22	Compressibility coefficient
BHT	1-10	Bibliography on High Temperature Chemistry and Physics of Materials in the Condensed State
BHTG	1-10	Bibliography on High Temperature Chemistry and Physics of Gases and Gas-condensed Phase Reactions
BIB	1-22	Bibliography
BTR	1-10	Battelle Technical Review
B1	1-240	Crystal structure notation: face - centered cubic

C

Symbol	Page	Explanation
c	1-59	Velocity of light
c	1-179	Lattice parameter
C	1-3	Carbon
C	1-56	Third Term in equation $C_p = A + BT + CT^{-2} + DT^2$
C		Centigrade (used with ° or deg)
$C_p^\circ$	1-25	Heat capacity; additional identifying subscripts may be used; usually units will be cal deg K <sup>-1</sup> gfw <sup>-1</sup> ; the superzero indicates material is in its standard state
$C_v$	1-90	Heat capacity at constant volume
Ca	1-3	Calcium
CA	1-9	Chemical abstract; also expressed as C. A.
cal	1-25	Calorie i. e., (thermochemical calorie); as noted on 1-33, one thermochemical calorie = 4.184 absolute joules
CCP	1-10	Current Chemical Papers
Ce	1-3	Cerium
CE	1-10	Ceramics abstracts
CEMP	1-22	Condensed phase: electric or magnetic property
COPT	1-22	Condensed phase: optical property
COTS	1-10	Consolidated Translation Survey
CPH	1-22	High-temperature heat capacity
CPL	1-22	Low-temperature heat capacity
Cr	1-3	Chromium
CRYS	1-22	Crystal structure

C (Concl'd)

Symbol	Page	Explanation
CT	1-10	Chemical Titles
CTEX	1-22	Coefficient of thermal expansion
C1	1-201	Crystal structure notation: face-centered cubic
C32	1-310	Crystal structure notation

D

d	1-191	Density
D	1-56	Fourth Term in equation: $C_p = A + BT + CT^{-2} + DT^2$
D	1-356	Dissociation energy
D	1-448	Debye function
$D_e$	1-39	Spectroscopic constant for diatomic molecule known as stretching constant; see page 1-78 for further definition
$D_e$	1-57	Dissociation energy relative to minimum of potential curve
$D_o$		Dissociation energy relative to lowest vibrational level
$D_v$	1-78	Mean rotational constant or stretching constant; this differs only slightly from $D_e$ above (p. 1-39)
$D_{\infty h}$	1-279	Group theory symbol to designate type of symmetry possessed by a molecule
$D_{6h}^4$	1-298	Space group
$^1D$	1-209	Designation of an electronic state for an atom
DA	1-10	Dissertation abstracts; also appears as Diss. Abst.

D (Concl'd)

Symbol	Page	Explanation
deg		Degree (most often Kelvin but also Centigrade or Fahrenheit)
DF	1-22	Free-energy of formation, reaction, etc.
DH	1-22	Heat of formation, reaction, etc.
DHD	1-22	Dissociation energy
DHT	1-22	Heat of transformation
DTIE	1-18	Division of Technical Information Extension
Dy	1-3	Dysprosium
D5	1-286	Crystal structure notation: body-centered cubic

E

E	1-22	Internal energy
E	1-39	Energy level of given electronic state relative to zero point state in $\text{cm}^{-1}$ (Herzberg's $\nu_{00}$ ) <sup>*</sup>
E	1-108	Activation energy
E	1-447	Einstein function
EI	1-10	Engineering Index
ELCH	1-22	Electrochemical
EMF	1-22	Electromotive force
ERES	1-22	Electrical resistivity
e. u.	1-22	Entropy unit; identically $\text{cal deg K}^{-1} \text{ gfw}^{-1}$
e. v.		Electron volt

<sup>\*</sup>Herzberg, G., Molecular Spectra Molecular Structures, I. Spectra of Diatomic Molecules, Van Nostrand, New York (1950).

F

Symbol	Page	Explanation
f		Formation, (usually subscript; e. g., $\Delta H_f^\circ$ )
f(r)	1-57	Function of internuclear distance
F	1-22	Free-energy function
F	1-58	Function defined and used only on this page (p. 1-58)
F	1-120	Fahrenheit (used with ° or deg)
$-\left(\frac{F_T^\circ - H_0^\circ}{T}\right)$	1-193	Free-energy function relative to 0°K
$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	1-36	Free-energy function relative to 298.15°K; sometimes abbreviated fef
fcc	1-335	Face-centered cubic
f. e. . or (fef)	1-64	Free-energy function; i. e., $-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)$

G

g	1-39	Degeneracy
g		Gram
g		Abbreviation for gas; often used as subscript
G	1-58	Function defined and used only on this page (p. 1-58)
Gd	1-3	Gadolinium
gfw	1-25	Gram formula weight; or molecular weight
gm		Gram
GPO	1-25	U. S. Government Printing Office
GR	1-10	U. S. Government Research Reports

## H

Symbol	Page	Explanation
H	1-22	Heat content
$H_T^\circ - H_{298}^\circ$	1-36	Heat content at $T^\circ\text{K}$ minus heat content at $298.15^\circ\text{K}$
$H_{298}^\circ - H_0^\circ$	1-25	Heat content at $298.15^\circ\text{K}$ minus heat content at $0^\circ\text{K}$
hcp	1-335	Hexagonal close-packed
Hf	1-3	Hafnium

## I

i	1-494	Isotopic abundance correction factor
I	1-434	Moment of inertia
I	1-494	Ion-beam current in mass spectrometer
$I_x$	1-234	Moment of inertia about x-axis
$I_y$	1-234	Moment of inertia about y-axis
$I_z$	1-235	Moment of inertia about z-axis
$I^+$	1-364	Ion-beam current in mass spectrometer
$I_A I_B I_C$	1-40	Product of moments of inertia
$I_x I_y I_z$	1-229	Product of moments of inertia
Ir	1-3	Iridium
IUPAC	1-10	International Union of Pure and Applied Chemistry

## J

J	1-267	Inner quantum number for atom or ion
JANAF	1-13	Joint Army Navy Air Force; thermochemical tables prepared by Dow Chemical Company Midland, Michigan

K

Symbol	Page	Explanation
K	1-25	If written as °K, or deg K, it implies degrees Kelvin
K	1-90	Lindemann constant; a value of $K = 137$ was used here
$k_e$	1-57	Force constant
$K_p$	1-36	Equilibrium constant at constant pressure; on page 1-36, $K_p$ represents equilibrium constant for the formation reaction from pure elements
$k_1$	1-59	Force constant for stretching
$(k_\delta / \ell^2)$	1-59	Bending force constant
$(k_\Delta / \ell^2)$	1-62	Bending force constant
kcal	1-25	Kilocalorie
KIN	1-22	Kinetics
kx	1-252	Unit of length used in crystallography; almost equal to an angstrom

L

$\ell$	1-44	Used with subscripts on page 1-44 to indicate seven constants for representing thermal data
$\ell$		Liquid; often used as a subscript for element or compound
$l$	1-59	Internuclear distance when used with bending-force constant
La	1-3	Lanthanum
LAMS	1-17	Los Alamos Scientific Report
L. C.	1-96	Lindemann constant
L'3	1-295	Crystal structure notation

M

Symbol	Page	Explanation
$M_i$	1-90	Molecular weight of $i^{\text{th}}$ element
$M_M$	1-60	Mass of metal atom expressed in grams
$M_O$	1-60	Mass of oxygen atom expressed in grams
Mg	1-3	Magnesium
MISC	1-22	Miscellaneous
M. I. T.	1-17	Massachusetts Institute of Technology
Mn	1-3	Manganese
Mo	1-3	Molybdenum
MPP	1-22	Miscellaneous physical properties
MSP	1-22	Mass-spectrometric data

N

$n$	1-57	Parameter defined on page 1-57
N	1-33	Avogadro number
N	1-3	Nitrogen
$n_c$	1-58	Column number in periodic table; used only on page 1-58
$n_r$	1-58	Column number in periodic table; used only on page 1-58
Nb	1-3	Niobium
Nd	1-3	Neodymium
NRC	1-277	National Research Council
NS or NSA	1-9	Nuclear Science Abstracts
NSA or NS	1-9	Nuclear Science Abstracts



O

Symbol	Page	Explanation
O	1-3	Oxygen
Os	1-3	Osmium

P

P	1-115	Pressure
PA	1-9	Physics Abstracts
PHAS	1-22	Phase data, melting, transition, boiling temperatures
PMCH	1-22	Mechanical properties
Pt	1-3	Platinum

R

r	1-57	Internuclear distance for diatomic molecule
R	1-33	Gas constant
$r_e$	1-57	Internuclear distance for diatomic molecule at the equilibrium displacement
RA	1-10	Monthly Index of Russian accessions
RAD		Research and Advanced Development Division of Avco Corporation
Re	1-3	Rhenium
reac		reaction (usually used as subscript; e. g. , $\Delta H^\circ_{\text{reac}}$ )
REAC	1-22	Chemical reaction
REV	1-22	Review
Rh	1-3	Rhodium
RHO	1-22	Density
RTD	1-135	Research and Technology Division, Dayton, Ohio

S

Symbol	Page	Explanation
s		Solid, often used as subscript to designate state of an element or compound; sublimation, occasionally used as subscript to indicate sublimation
S	1-22	Entropy
S	1-493	Sensitivity of mass spectrometer; electron multiplier conversion factor
$S_T^\circ$	1-36	Entropy at $T^\circ\text{K}$ for material in its standard state
$S_{298}^\circ$	1-25	Entropy of substance in standard state at $298.15^\circ\text{K}$ measured in $\text{cal deg K}^{-1} \text{ gfw}^{-1}$ ; i. e., e. u.
ls	1-209	Designation of electronic state for an atom
Sc	1	Scandium
Si	1-3	Silicon
Sm	1-3	Samarium
SPK	1-22	Spectroscopic data
Sr	1-3	Strontium
sub		Sublimation; most often used as subscript to designate a sublimation (occasionally vaporization) process
SURF	1-22	Surface properties

T

t	1-120	Temperature; on page 1-120 units are degrees Fahrenheit
t	1-194	Temperature; on page 1-194 units are degrees centigrade
T	1-25	Temperature, absolute; unless otherwise stated to be expressed in degrees Kelvin; subscripts may be used further to identify temperature; e. g., $T_1$ on page 1-25 means temperature of first transition

T (Concl'd)

Symbol	Page	Explanation
T <sub>b</sub>	1-36	Temperature of boiling
T <sub>c</sub>	1-88	Melting point of compound
T <sub>e</sub>	1-267	Energy term value for a diatomic molecule; relative to bottom of potential energy curve
T <sub>i</sub>	1-88	Melting point of element i
T <sub>m</sub>	1-36	Temperature of melting
T <sub>t</sub>	1-36	Temperature of transition
Ta	1-3	Tantalum
TAB	1-10	Technical Abstract Bulletin
Tc	1-3	Technetium
TCON	1-22	Thermal conductivity
Th	1-3	Thorium
THEO	1-22	Theory
THER	1-22	Thermodynamic data
Ti	1-3	Titanium
Trans	1-287	Transition or transformation (used as subscript)
TRT	1-22	Transformation temperature
TT	1-10	Technical Translations

U

U	1-3	Uranium
UCRL	1-307	University of California Radiation Laboratory

V

Symbol	Page	Explanation
v	1-78	Vibrational quantum number
v	1-191	Atomic volume
V	1-3	Vanadium
V	1-57	Potential energy
$V_i$	1-90	Atomic volume
vap		Vaporization; most often used as a subscript to designate a vaporization (occasionally sublimation) process
VAP	1-22	Vaporization data

W

W	1-3	Tungsten
WADC	1-13	Wright Air Development Center, Ohio
WADD	1-14	Wright Air Development Division, Ohio

X

x	1-251	Used to represent the number of atoms in a molecule; for nonstoichiometric compounds, $x$ need not be a whole number
X	1-67	Spectroscopic symbol to designate ground electronic state, usually written to precede the symbol for the state; e. g., $X^3\Pi$
$x_e \omega_e$	1-58	Anharmonicity constant often written as $\omega_e x_e$

Y

Symbol	Page	Explanation
y	1-251	Represents number of atoms in a molecule; nonwhole numbers are possible for nonstoichiometric compounds
Y	1-3	Yttrium
Y	1-193	Young's modulus

Z

ZKP	1-22	Equilibrium constant
Zr	1-3	Zirconium

Greek Symbols

$\alpha$  -- alpha

$\alpha$	1-60	Angle formed by atoms of a molecule
$\alpha$	1-111	Designation of a particular crystal modification
$\alpha_e$	1-39	Spectroscopic constant for diatomic molecule; the vibrational-rotational coupling constant; see page 1-78 for definition

$\beta$  -- beta

$\beta$	1-111	Designation of a particular crystalline modification or phase
$\beta$	1-192	Compressibility
$\beta_e$	1-78	Higher-order correction term to stretching constant, $D_e$

$\gamma$  -- gamma

Symbol	Page	Explanation
$\gamma$	1-111	Designation of a particular crystalline modification or phase
$\gamma$	1-192	Coefficient for the linear-temperature terms used in low-temperature expansion (mathematic) of heat capacity
$\gamma_e$	1-78	Spectroscopic constant for diatomic molecule; this term is a higher-order correction to $B_e$

$\delta$  or  $\Delta$  -- delta

$\delta$	1-58	Parameter in equation (IIIB. -9); not used elsewhere in text
$\delta$	1-112	Designation of a particular crystal modification
$\Delta$	1-67	Designates electronic state of a diatomic molecule (usually has arabic numeral as a left-hand superscript)
$\Delta$	1-226	Differences as defined on this page; i. e., p. 1-226
$\Delta C_p^\circ$	1-301	Net change in heat capacity for a chemical reaction
$\Delta(f. e. f.)$	1-64	For a given reaction, the weighted sums of the free-energy functions for products minus the weighted sums of the free-energy functions for the reactants
$\Delta F_f^\circ$	1-36	Standard free energy of formation
$\overline{\Delta F}$	1-287	Relative partial molar free energy (Gibbs); may appear as $\overline{\Delta G}$ when quoted
$\Delta H^\circ$	1-99	Heat of reaction; i. e., change in heat content
$\Delta H_f^\circ$	1-36	Standard heat of formation
$\Delta H_m$	1-36	Heat of melting (at $T_m$ on page 1-36) called $\Delta H_{\text{fusion}}$ on page 1-158

$\delta$  or  $\Delta$  -- delta (Concl'd)

Symbol	Page	Explanation
$\Delta H_{f,0}^\circ$	1-36	Standard heat of formation 0°K
$\Delta H_{f,298}^\circ$	1-25	Standard heat of formation at 298.15°K
$\Delta H_s^\circ$ or $\Delta H_{sub}^\circ$	1-36	Heat of sublimation at given temperature
$\Delta H_t$	1-36	Heat of transition (at $T_t$ on page 1-36) (see also below)
$\Delta H_{Trans}$	1-287	Heat of transition at temperature (see immediately above)
$\Delta H_v$ or $\Delta H_{vap}$	1-36	Heat of vaporization (at $T_v$ on page 1-36)
$\Delta r$	1-57	Displacement from equilibrium separation for diatomic molecule; i. e., $\Delta r = r - r_e$
$\Delta S$	1-99	Change in entropy
$\Delta S_f^\circ$	1-64	Standard entropy change

$\epsilon$  -- epsilon

$\epsilon$	1-332	Represents a particular phase (i. e., crystal form)
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$\theta$  -- theta

$\theta$	1-228	Symmetry number; also see $\sigma$
$\theta_i$	1-90	Debye temperature for $i^{th}$ element in degrees Kelvin
$\theta_i'$	1-90	Effective Debye temperature for $i^{th}$ element in the compound state

$\lambda$  or  $\Lambda$  -- lambda

Symbols	Page	Explanation
$\lambda$	1-25	Heat of a phase change; a subscript may be used for further identifications; alternatively, $\Delta H$ with appropriate subscript may also be used to represent the heat of a phase change
$\Lambda$	1-266	Component of angular momentum along internuclear axis

$\mu$  -- mu

$\mu$	1-59	Reduced mass of molecule in atomic mass units
$\mu$	1-192	Shear modulus

$\nu$  -- nu

$\nu$	1-78	Energy level in $\text{cm}^{-1}$
$\nu_e$	1-348	Energy level in $\text{cm}^{-1}$

$\pi$  -- pi

$\pi$	1-50	3.14159
$\pi$	1-67	Designates electronic state: e. g., $^3\pi$

$\sigma$  or  $\Sigma$  -- sigma

$\sigma$	1-40	Symmetry number, see also $\theta$
$\sigma$	1-192	Poisson's ratio



$\sigma$  or  $\Sigma$  -- sigma (Concl'd)

Symbol	Page	Explanation
$\sigma$	1-493	Cross section for ionization of neutral species
$\Sigma$	1-67	Designates electronic state of a molecule; e. g., $^1\Sigma$
$\Sigma$	1-266	Component of electron spin along internuclear axis

$\omega$  -- omega

$\omega$	1-40	Vibrational frequencies for polyatomic molecule; subscripts may be used as shown on page 1-60 to identify a particular frequency
$\omega_e$	1-39	Vibrational frequency for diatomic molecule
$\omega_e x_e$	1-39	Anharmonicity constant
$\omega_e y_e$	1-39	Anharmonicity constant of higher order than $\omega_e x_e$ , see page 1-78

## I. INTRODUCTION AND GUIDE TO USE OF THIS WORK

### A. GENERAL DESCRIPTION

The present work, contract AF33(657)-8223, is a continuation and modification of an earlier contract, AF33(616)-7327. Results of the earlier work have been summarized in the final report for that project.<sup>1</sup> For the present work, thermodynamic properties have been obtained for a selected group of refractory compounds in the range from 0° to 6000°K. This work has involved both theoretical analyses and experimental spectroscopic studies.

The class of compounds studied includes the borides, carbides, nitrides, and oxides of some elements in groups IIA, IIIB, IVA, IVB, VB, VIB, VIIB, and VIII as well as selected elements from the rare-earth and actinide series. The group of elements studied is given in figure 1. All elements in the solid boxes are to be considered the metallic elements under consideration, and those in the broken box are the nonmetals. Thus, silicon borides, carbides, nitrides, and oxides are investigated, and compounds such as chromium silicides are not investigated. An alphabetic listing of all elements being studied is shown in table 1.

The present work is devoted to the preparation of thermodynamic tables as illustrated by the tables in section VII. They follow the general format used in tables of the final report of the earlier project.<sup>1</sup> As far as possible, these tables are also compatible with the JANAF tables.<sup>2</sup> The tables from this work are all located in section VII, volume 2.

To accomplish the work objectives, two phases of the current project are defined:

Phase I    Review of the literature,

Phase II    Analysis of data, and calculation and tabulation of thermodynamic properties.

For Phase I, basic data have been abstracted from the literature as completely as possible. A partial list of subjects used as a guide in the selection of references is given on the following page:

1. Phase diagrams,
2. Heat capacity versus temperature,
3. Enthalpy versus temperature,
4. Entropy versus temperature,
5. Heat of phase transformations,
6. Heat of formation or reaction,
7. Thermal-expansion coefficient and compressibility,
8. Melting and triple points,
9. Free energy of formation,
10. Vapor pressure,
11. Composition of vapor species,
12. Spectroscopic constants,
13. Ionization or appearance potentials,
14. Electromotive force of electrolytic cells,
15. Heat of solution or dilution, and
16. Other thermodynamic functions.

The work for Phases I and II has been conducted in a pattern similar to that employed in the previous project.<sup>1</sup>

Some aspects of the literature review (Phase I) are discussed in section IIB (Information Processing). Actual bibliography references for particular compounds are discussed in the appropriate portions of Section IV, Data Reviews and Computation Summaries for Individual Elements and Compounds. A comprehensive bibliography has also been compiled on IBM cards and is illustrated in sections VIII and IX (Volume 2).

The work for Phase II has involved thorough reviews and analyses of pertinent thermodynamic data. The actual reviews and analyses are given in section IV. Thermodynamic tables prepared following the analyses are consolidated in Section VII, Thermodynamic Tables (Volume 2).

IIA	IIIB	IVB	VB	VIB	VII B	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA		
4													I		
Be													H		
12													9		
Mg													F		
20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
		58	59	60	61	62	63	64	65	66	67	68	69	70	71
		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		90	91	92	93	94	95	96	97	98	99	100	101	102	
		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	

**Figure 1** AREAS OF PERIODIC CILAR INCLUDING ELEMENTS WHOSE COMPOUNDS ARE THE SUBJECT OF THE PROJECT (ELEMENTS IN SOLID BOXES COMBINED WITH THOSE IN BROKEN BOX)

In section V is presented a discussion of the need for cooperation between scientific groups to expedite accumulation of scientific data.

Recommendations resulting from both phases of this project are presented in section VI.

TABLE I

ALPHABETIC LISTING OF ELEMENTS

Symbol	Element	Symbol	Element
B	Boron	O	Oxygen
Be	Beryllium	Os	Osmium
C	Carbon	Pt	Platinum
Ca	Calcium	Re	Rhenium
Ce	Cerium	Rh	Rhodium
Cr	Chromium	Sc	Scandium
Dy	Dysprosium	Si	Silicon
Gd	Gadolinium	Sm	Samarium
Hf	Hafnium	Sr	Strontium
Ir	Iridium	Ta	Tantalum
La	Lanthanum	Tc	Technetium
Mg	Magnesium	Th	Thorium
Mn	Manganese	Ti	Titanium
Mo	Molybdenum	U	Uranium
N	Nitrogen	V	Vanadium
Nb	Niobium	W	Tungsten
Nd	Neodymium	Y	Yttrium
		Zr	Zirconium

## REFERENCES FOR SECTION IA

1. Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, 2 Vols., ASD TR 61-260, Pt. I (May 1962).
2. Stull, D. R. et al, JANAF Thermochemical Tables, Dow Chem. Co., Midland, Mich. (1960-1964).

## B. QUICK GUIDE TO WORK ACCOMPLISHED

Several possible methods of using the data in this work are possible, depending on the needs of the investigator. To find material in this work may be difficult unless the arrangement is detailed. An attempt is made to illustrate the arrangement by a series of questions which a harassed investigator may ask when he turns to his work

### 1. What Elements or Compounds Are Contained Here?

Data for 31 metallic elements and their compounds (borides, carbides, nitrides, and oxides) have been obtained. Lists of the elements and compounds are shown in the table of contents for section IV, or figure 1 and table 1 of section IA.

### 2. Which Elements or Compounds Have Been Critically Analyzed?

The elements and the compounds which have been analyzed are listed in the table of contents for sections IVA and IVB, respectively. Under a given compound group, it may be noted that the arrangement is in the following order: borides, carbides, nitrides, and oxides.

For a very rapid check on available data, one can refer to table 2.

### 3. Have Tables Been Prepared for All Elements and Compounds Which Have Been Critically Analyzed?

Yes.

### 4. How Can a Table for a Given Element or Compound Be Located?

All the tables (0° to 6000°K) are in section VII (Volume 2). They are arranged in the same manner as JANAF tables. A complete explanation of the arrangement is at the beginning of section VII. Basically, the tables are arranged in alphabetic order with compound symbols also arranged alphabetically. Thus, HfO is arranged as HfO, but TiO is arranged as OTi.

One can also locate a given table by reference to the table of contents or the list at the start of section VII.

5. What Is the Purpose of the Back Sheets of the Thermodynamic Tables?

The back sheets follow the JANAF format; their purpose is to give a very brief account of the basic data used to develop a table. However, the complete analyses in section IV must be consulted if more details are required.

6. What Is the Purpose of the Uncertainty Estimates?

The present thermodynamic tables have been calculated to three places beyond the decimal point. Usually however, the actual data are not this accurate. The uncertainty estimates are intended to alert the user to the possible accuracy of the numbers tabulated.

7. If Data Analyses and Tables Have Not Been Prepared for a Given Element or Compound, Is There Any Possible Information Available?

Yes. A bibliography (Volume 2) for the 31 metals and 4 nonmetals already referred to has been maintained. References to the property file (section IX) and then to the bibliography (section VIII) may lead one to references of interest for a particular compound.

TABLE 2  
FINAL STATUS OF THERMODYNAMIC TABLES

[illegible]

These tables were prepared in the present project, they also appear in Volume 2, this work. Discussions are given in b.4 & three

These tables originally appeared in Kuratalt, I. et al.  
: Thermodynamics of Certain Helvetic Compounds, in: I. and I.  
ASD 74-61-266 (Nov. 1962), they now appear in volume 6, this work



## II. FUNDAMENTAL PROCEDURES: INFORMATION PROCESSING, CHOICE OF PHYSICAL CONSTANTS, AND THERMODYNAMIC TABLE FORMAT

### A. GENERAL

In a project of this nature, it is desirable to maintain a high degree of internal consistency. That is, consistent sets of physical constants and uniform methods of evaluating data, etc., are needed. Some of the procedures adopted for reviewing the mushrooming technical literature have now been standardized. Different aspects of the literature problem are discussed first.

## B. INFORMATION PROCESSING

### 1. Review of Unclassified Literature

For the current project, it was necessary to continue and expand the literature search of the previous contract.<sup>1</sup> Additional elements were included which were not covered originally. Cerium, iridium, platinum, thorium, and rhodium were added at a later stage of the previous contract and were not entirely completed. Uranium and the rare earths were additional elements not previously included.

Hence, one portion of the literature search has been to review the older literature to the present for the elements listed in the paragraph immediately above. A second aspect of the literature search has been to study recent literature (1961 to present) for all of the elements included in this project and the previous one.

An indication of the scope of the literature search is shown by the accompanying list of literature sources. This list is divided into three categories. The first lists abstracting-type journals which have been utilized, the second lists current periodicals received at Avco RAD for review, and the third lists compilations, books, and review articles. In the list of 21 abstracting sources, the arrangement is in order of decreasing utility, but the first 14 of such references have been routinely consulted, and the remaining 7 with varying degrees of regularity.

Chemical Abstracts is probably the most important single source of thermodynamic data, and hence, an effort has been made to keep its review up to date for all 35 elements and compounds of interest. For the bibliography (section VIII) of this work, Chemical Abstracts through October 1963 has been reviewed. Nuclear Science Abstracts has been reviewed for the older literature and to early 1963. The other abstracting services have received partial coverage in 1963. Thus, Technical Abstract Bulletins (TAB) and Chemical Titles have been consulted to obtain recent Governmental reports and periodical references, respectively, during 1963 for the 10 elements (and their compounds) being emphasized during the most recent parts of this project. The 10 elements are Zr, Hf, Ta, W, Nb, Ti, Mo, Th, Be, and Si.

#### Current Literature--Abstracts

(Abbreviations Follow References)

1. Chemical Abstracts -- CA
2. Nuclear Science Abstracts -- NSA or NS
3. Physics Abstracts -- PA

4. IUPAC--Subcommission on Condensed States. Bibliography on High-Temperature Chemistry and Physics of Materials in the Condensed State--Quarterly Reviews --BHT
5. IUPAC--Subcommission on Gases. Bibliography on High-Temperature Chemistry and Physics of Gases and Gas Condensed Phase Reactions--L. Brewer--Quarterly Reviews --BHTG
6. Consolidated Translation Survey--Foreign Documents Division--Central Intelligence Agency, Washington 25, D. C. --COTS
7. Monthly Index of Russian Accessions (Library of Congress)--RA
8. Current Contents--Weekly Issues--Institute for Scientific Information, Philadelphia
9. Current Chemical Papers--Monthly Issues--The Chemical Society, London--CCP
10. Technical Abstract Bulletin--Twice Monthly Issues--Alexandria, Virginia--TAB
11. Chemical Titles--Twice Monthly Issues--American Chemical Society, Easton, Pennsylvania--CT
12. Bulletin of Chemical Thermodynamics and Thermochemistry--IUPAC--Commission on Thermodynamics and Thermochemistry No. 5--1962 and Earlier Numbers
13. American Society for Metals -- Review of Metal Literature --ASM
14. Monthly Catalog of U. S. Government Publications
15. Solid State Abstracts
16. Ceramics Abstracts -- CE
17. Technical Translations -- TT
18. U. S. Government Research Reports --GR
19. Battelle Technical Review -- BTR
20. Dissertation Abstracts -- DA
21. Engineering Index -- EI.

Current Literature--Received Regularly at Avco RAD for Review

1. Acad. Sci. --Dokl. Akad. Nauk SSSR--Physical Chemistry Section
2. Acta Cryst.
3. Acta Met.
4. Am. Ceram. Soc., J.
5. Am. Chem. Soc., J.
6. Am. Phys. Soc. Bull.
7. Astrophys. J.
8. Chem. Revs.
9. Cum. Book Index
10. Electrochem. Soc., J.
11. Faraday Soc. Trans.
12. Inst. Metals, J.
13. J. Chem. Phys.
14. J. Chim. Phys.
15. J. Metals
16. J. Mol. Spectr.
17. J. Phys. Chem.
18. J. Res. Natl. Bur. Std.
19. J. Less-Common Metals
20. Mol. Phys.
21. Natl. Acad. Sci., U. S., Proc.
22. Nature
23. Opt. Soc. Am., J.

24. Opt. Spectr.
25. Physica
26. Phys. Rev.
27. Phys. Soc., Japan., J.
28. Phys. Soc. (London), Proc.
29. Phys. Chem. Solids, J.
30. Phys. Fluids
31. Phys. Metals Metallog.
32. Planetary Space Sci.
33. Rev. Sci. Instr.
34. Rev. Mod. Phys.
35. Russ. J. Phys. Chem.
36. Russ. Tech. Lit.
37. Science
38. Soviet Phys. "Doklady"
39. Soviet Phys. JETP
40. Soviet Phys. Solid State
41. Soviet Phys. Tech. Phys.
42. Z. Anorg. Allgem. Chem.
43. Z. Elektrochem.
44. Z. Physik.
45. Physik. Chem. (Neue Folge)
46. In addition, periodical literature at the Massachusetts Institute of Technology; Cambridge Research Laboratories Library, Hanscom Field; and other regional libraries is also reviewed.

### Compilations, Books, and Review Articles

1. Skinner, H. A., Experimental Thermochemistry, Vol. 2, Interscience, New York (1962).
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2. Review of Classified Literature

To review classified Atomic Energy Commission (AEC) literature, visits were made to the New York AEC library and the Oak Ridge library of the Division of Technical Information Extension (DTIE). The review at the Oak Ridge installation was made in April 1963 and covered literature available in 1961-1962.

In general, it has been concluded that there is only a small amount of thermodynamic data in the classified literature which is not already unclassified. In view of the problems of classification, and because of the small proportion of useful data, no effort has been made to incorporate the classified data into thermochemical tables for this project.

For those with a need to know, the Abstracts of Classified Reports (ACR) published by DTIE is probably the best means to locate useful classified literature on thermodynamic data.

3. Method of Compiling Bibliography

In making the literature review, reference data were first tabulated on an ASM punched card. A serial number was then assigned this reference and was located in the upper right-hand corner of the ASM card. Ordinarily, the ASM card carried the author's name, company or university affiliation (if known), title of article, journal reference, and any abstracting references. A note or abstract from the article might also be included on the original ASM card.

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[illegible]

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LA 55, 722 (1964)	200767
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SINILCO, I. PHASES OF TITANIUM CARBIDE FOR SYSTEMS CONSISTING OF GROUP IV ELEMENTS AND OXYGEN THERMAL STABILITY AND KINETICS OF OXIDATION CHIM 10, 17 (1963) CA 55, 717 (1961)	200769 200770 200771 200772 200773 200774
SLIGHTER, J. PRECISELY DETERMINED PARAMETER DETERMINATION OF ZIRCONIUM-OXYGEN SOLUBILITY TRANSLATION OF J. CHEM. PHYS. 30, 1012 (1960) CA 55, 6961 (1961)	200774 200775 200776 200777 200778
SOAFA, J. MAGNETIC TRANSITION IN TITANIUM J. CHEM. PHYS. 30, 1012 (1960) CA 55, 6961 (1961)	200764 200765 200766 200767
SAMSONOV, G. YA AND V. G. SMILLO, E. THE REACTION OF CERTAIN CARBIDES WITH REFRACTORY METALS AT HIGH TEMPERATURES J. CHEM. PHYS. 30, 1012 (1960) CA 55, 6961 (1961)	100180 100181 100182 100183 100184
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SMILLO, E. THEORY OF GASEOUS CARBONIZATION IN THE SILICON-CARBIDE BINARY SYSTEM SILICON CARBIDE POLYMERIZATION 1959, 24 (1960) CA 55, 714 (1961)	200771 200772 200773 200774 200775
TAYLOR, R. AND J. J. CRYSTAL STRUCTURE AND THERMAL EXPANSION OF CUBIC AND HEXAGONAL TITANIUM CARBIDE SILICON CARBIDE POLYMERIZATION 1959, 24 (1960) CA 55, 6977 (1961)	200776 200777 200778 200779 200780
TAYLOR, R. AND J. J. CRYSTAL STRUCTURE AND THERMAL EXPANSION OF CUBIC AND HEXAGONAL TITANIUM CARBIDE SILICON CARBIDE POLYMERIZATION 1959, 24 (1960) CA 55, 6977 (1961)	200776 200777 200778 200779 200780
TAYLOR, R. AND J. J. CRYSTAL STRUCTURE AND THERMAL EXPANSION OF CUBIC AND HEXAGONAL TITANIUM CARBIDE SILICON CARBIDE POLYMERIZATION 1959, 24 (1960) CA 55, 6977 (1961)	200776 200777 200778 200779 200780



Sample (Concl'd)

PAKMAN DETECTOR OF THE AUTOMATIC 120	200760
TRANS FARMWAY 22 500 1207 (1960)	200760
A 55, 1204 (1961)	200760

## Property Definition Sheet

DEFINITIONS FOR PROPERTY(SUBJECT) FILE JUNE 27, 1962

BETA	COMPRESSIBILITY COEFF (BETA = 1/V * (DV/DPT)
BIP	BIPOLAROGRAPHY
CEMP	CONDENSED PHASE, ELEC OR MAGNETIC PROP, EQ WORK FUNC
COPT	CONDENSED PHASE, OPTICAL PROP.
CPH	HIGH TEMPERATURE HEAT CAPACITY
CPL	LOW TEMPERATURE HEAT CAPACITY
CRYS	CRYSTAL STRUCTURE
CTEX	COEFF OF THERMAL EXPANSION
DE	FREE ENERGY OF FORMATION, REACTION, ETC.
DN	HEAT OF FORMATION, REACTION, ETC.
DND	DISSOCIATION ENERGY
DHT	HEAT OF TRANSFORMATION
E	INTERNAL ENERGY
ELCH	ELECTROCHEMICAL
EMF	ELECTROMOTIVE FORCE
EREE	ELECTRICAL RESISTIVITY
F	FREE ENERGY FUNCTION
H	HEAT CONTENT
KIN	KINETICS
MISC	MISCELLANEOUS
MOP	MISCELLANEOUS PHYSICAL PROPERTIES
MSP	MASS SPECTROSCOPIC DATA
PHAS	PHASE DATA, MELTING, TRANSITION, BOILING TEMP
PMCH	MECHANICAL PROPERTIES
REAC	CHEMICAL REACTIONS
REV	REVIEW
RH2	DENSITY
S	ENTROPY
SPK	SPECTROSCOPIC DATA
SURF	SURFACE PROPERTIES
TC2N	THERMAL CONDUCTIVITY
THE2	THERPY
THFR	THERMODYNAMIC DATA
TRT	TRANSFORMATION TEMPERATURE
VAP	VAPORIZATION DATA
ZKP	EQ CONST

# Property File Sheet

①	②	④	⑤		
SPK	TC	61	700954	MPP TH	
③ SHADMI, Y				MURRAY, J	58 601094
THER TC				MPP TH	
SCHICK, H ANTHROP		62	300995	SMITH, J	58 601073
THER TC				MPP TH	
MARGRAVE, J		61	700967	SKINNER, G BECKETT	50 601226
TRT TC				PHAS TH	
SZABO, Z LAKATOS		62	601673	ANON	62 601629
SPK TC F 6				PHAS TH	
CLAASSEN, H SELIG		62	201854	ANON	57 601305
THER TC O				PHAS TH	
SCHICK, H ANTHROP		62	300996	WILSON, W AUSTIN	58 601071
DN TE				PHAS TH	
WHITE, D		61	201217	VON BOLTON, W	08 800117
SPK TE				PHAS TH	
NORRIS, J		60	601194	MARDEN, J RENTSCHL	27 900119
REAC TE C				PHAS TH	
TRZEBIATOWSKI, W		62	201857	SCHULTZE, A	30 900117
BIB TH				PHAS TH	
DAVID, L		53	600957	BADAEVA, T	61 201890
CRYS TH				REAC TH	
AMONENKO, V VASYUT		63	301170	DEYE, R	50 601156
CEMP TH				REAC TH	
FRANCIS, E		58	601536	DEUTSCH, N ERVIN	60 500123
CEMP TH				REAC TH	
MESMARD, G UYAN, R		51	400558	MURRAY, J	58 601094
CEMP TH				REV TH	
RIVIERE, J		62	201806	KAUFMANN, A	62 601429
CPH TH				REV TH	
MITKINA, E		59	201029	ROLLEFSON, G HAGEM	51 601106

- Column ① - identifies the left-most column in heavy print on the first, alternate lines for a given reference. It refers to SPK, THER, THER, TRT, etc., on the sample page of the property file.
- Column ② - identifies the second or right-most column, in light print on the first, alternate lines for a given reference. It refers to TC, TC, etc., on the sample page of the property file.
- Column ③ - identifies the left-most column in light print on the second, alternate lines for a given reference. It refers to SHADMI, SCHICK, MARGRAVE, etc., on the sample page of the property file.
- Column ④ - identifies the middle column in heavy print in the second, alternate lines for a given reference. It refers to the last two digits of the year of publication, e. g. 61, 62, 61, etc.
- Column ⑤ - identifies the serial number on the right-most column on the second, alternate lines for a given reference. On the sample page of the property file, it is illustrated as 700954, 300995, 700967, etc.



The basic data on the ASM card being either handwritten or typewritten were transferred to IBM punched cards to achieve flexibility in operations. Whereas the earlier contract had also utilized IBM cards, it was observed that considerable effort was required to code literature references. For the present contract, a simplified procedure was adopted. Names of authors, titles, and journal references were spelled out directly, with no coding, in the compilation of the bibliography. The only coding retained was for the property file.

A sample bibliography, property definition sheet, and property file sheet are included in this section to illustrate the changes in format, but a complete property file and property definition sheet are shown in section IX (Volume 2). The complete bibliography (over 3000 references) arranged alphabetically is shown in section VIII (Volume 2).

Ordinarily to use these files, one consults the property file first to locate the element or compound of interest. This information is found in column 2 of the property file. In column 1 of the property file is a 4-letter (or less) code for the property of interest. Definitions of these codes are to be found in the property definition sheet. Thus, CPH is high-temperature heat capacity (i. e., above 298.15°K). If a particular compound and a property are located in the property file, one then uses the author information and year in columns 3 and 4 to locate the desired reference in the alphabetic bibliography (section VIII). If necessary, the numeric code (the six figures of the last columns of the property and bibliographic files) can be used in the final process of locating a reference in the alphabetic bibliography found in volume 2.

#### 4. Tabulation of Data

In a project of this scope, it is extremely important to maintain consistency and to use standard forms for tabulation of data, references, etc. For condensed phases, there are usually more varied types of data which must be considered. For these systems, a set of mimeographed forms has been developed which permits data to be tabulated as they are acquired. Because different references are acquired or reviewed at different times, these forms provide a single location for storage of such data. Then, when a definite review is desired, all of the pertinent data are available.

Copies of seven consecutive pages used as tabulation sheets for condensed phases are illustrated in figures 2 to 8. Use of these sheets should be self-explanatory; however, a few comments can be made. The purpose of the basic data sheet (figure 2) is to summarize the basic preferred data, used as input in the calculation of the tables. It should also be pointed out that sometimes, in this or succeeding compilation sheets, modifications may be necessary. For example, if  $C_p$  data are not available

**BASIC DATA**  
**CONDENSED PHASES**

NAME COMPD _____		FORMULA _____	REFERENCE	
MOI WT. _____			SECONDARY	ORIGINAL
$S_{298}^{\circ}$	_____ ± _____	e.u.		
$H_{298}^{\circ} - H_0$	_____ ± _____	cal/gfw		
$\Delta H_f^{\circ}, 298$	_____ ± _____	Kcal/gfw		
$\lambda_1(\text{transition})$	_____ ± _____	cal/gfw		
$T_1$	_____	°K		
$\lambda_2(\text{transition})$	_____ ± _____	cal/gfw		
$T_2$	_____	°K		
$\lambda(\text{melting})$	_____ ± _____	cal/gfw		
$T(\text{melting})$	_____	°K		
$C_{p, \text{solid}}^{\circ}$	_____	cal/degK-gfw		
	for _____ ≤ T ≤ _____ °K			
$C_{p, \text{solid}}^{\circ}$	_____	cal/degK-gfw		
	for _____ ≤ T ≤ _____ °K			
$C_{p, \text{liquid}}^{\circ}$	_____	cal/degK-gfw		
	for _____ ≤ T ≤ _____ °K			
ADDITIONAL DATA:				

Figure 2 BASIC DATA CONDENSED PHASES

COMPILATION SHEET NO. 1

A. CRYSTALLINE FORMS AND RANGE OF STABILITY			REFERENCE	
FORM (lowest temperature)	TEMPERATURE RANGE		SECONDARY	ORIGINAL
	FROM	TO		
_____ (preferred form)	_____ (preferred value)	°K		
_____	_____	_____		
_____	_____	_____		
_____	_____	_____		
_____	_____	_____		
_____	_____	_____		
_____	_____	_____		
_____	_____	_____		
REASON FOR CHOICE OF DATA: _____				
FORM NO. 2	_____ (preferred form)	_____ (preferred value)		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
REASON FOR CHOICE OF DATA: _____				
FORM NO. 3	_____ (preferred form)	_____ (preferred value)		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
	_____	_____		
REASON FOR CHOICE OF DATA: _____				

Figure 3 COMPILATION SHEET NO. 1

COMPILATION SHEET NO. 2

		REFERENCE	
		SECONDARY	ORIGINAL
<b>B. TEMPERATURES OF PHASE CHANGES</b>			
<b>1. TRANSITION TEMPERATURES</b>			
a. Lowest			
_____ °K (preferred value)			
_____			
_____			
_____			
_____			
REASON FOR CHOICE OF DATA: _____			
_____ °K (preferred value)			
_____			
_____			
_____			
_____			
REASON FOR CHOICE OF DATA: _____			
<b>2. MELTING TEMPERATURE</b>			
_____ °K (preferred value)			
_____			
_____			
_____			
_____			
_____			
REASON FOR CHOICE OF DATA: _____			

Figure 4    COMPILATION SHEET NO. 2

COMPILATION SHEET NO. 3

		REFERENCE	
		SECONDARY	ORIGINAL
<b>C. HEAT CHANGES</b>			
<b>1. HEAT OF FORMATION</b>			
	_____	±	_____ Kcal/gfw
	(preferred value)		
	_____	±	_____ Kcal/gfw
	_____	±	_____
	_____	±	_____
	_____	±	_____
	_____	±	_____
REASON FOR CHOICE OF DATA:		_____	
<b>2. HEAT OF TRANSITION</b>			
(at T = _____ °K)	$\lambda_1 =$	_____	±
	(preferred value)	_____	cal/gfw
	_____	±	_____
	_____	±	_____
	_____	±	_____
REASON FOR CHOICE OF DATA:		_____	
(at T = _____ °K)	$\lambda_2 =$	_____	±
	(preferred value)	_____	cal/gfw
	_____	±	_____
	_____	±	_____
	_____	±	_____
REASON FOR CHOICE OF DATA:		_____	
(at T = _____ °K)	$\lambda_{\text{melting}} =$	_____	±
	(preferred value)	_____	cal/gfw
	_____	±	_____
	_____	±	_____
	_____	±	_____
REASON FOR CHOICE OF DATA:		_____	

Figure 5 COMPILATION SHEET NO. 3

COMPILATION SHEET NO. 4

				REFERENCE	
				SECONDARY	ORIGINAL
<b>D. HEAT CAPACITIES</b>					
1. Low Temperatures					
{	$S_{298}^{\circ}$	_____ ± _____	e.u.		
	(preferred value)				
{	$H_{298}^{\circ} - H_0$	_____ ± _____	cal/degK-gfw		
	(preferred value)				
{	$C_p^{\circ}$	_____	cal degK-gfw from _____ to _____ °K		
	$C_p^{\circ}$	_____	cal degK-gfw from _____ to _____ °K		
	$C_p^{\circ}$	_____	cal degK-gfw from _____ to _____ °K		
	$C_p^{\circ}$	_____	cal degK-gfw from _____ to _____ °K		
	$C_p^{\circ}$	_____	cal degK-gfw from _____ to _____ °K		
	$C_p^{\circ}$	_____	cal degK-gfw from _____ to _____ °K		
{	$S_{298}^{\circ}$	_____ ± _____	e.u.		
	$H_{298}^{\circ} - H_0$	_____ ± _____	cal/degK-gfw		
{	$S_{298}^{\circ}$	_____ ± _____	e.u.		
	$H_{298}^{\circ} - H_0$	_____ ± _____	cal/degK-gfw		
{	$S_{298}^{\circ}$	_____ ± _____	e.u.		
	$H_{298}^{\circ} - H_0$	_____ ± _____	cal/degK-gfw		
METHOD OF SELECTING DATA					

Figure 6 COMPILATION SHEET NO. 4

COMPILATION SHEET NO. 5

		REFERENCE	
		SECONDARY	ORIGINAL
<b>D. HEAT CAPACITIES (Cont'd)</b>			
1. High Temperatures			
$\left\{ \begin{array}{l} C_{p1}^{\circ} = \text{_____} \text{ cal/}^{\circ}\text{K-gfw} \\ \text{for _____} \leq T \leq \text{_____} \\ C_{p2}^{\circ} = \text{_____} \text{ cal/}^{\circ}\text{K-gfw} \\ \text{for _____} \leq T \leq \text{_____} \\ C_{p3}^{\circ} = \text{_____} \text{ for liquid} \end{array} \right\}$			
$C_p^{\circ} = \text{_____} \text{ cal/}^{\circ}\text{K-gfw} \text{ for _____} \leq T \leq \text{_____}$			
$C_p^{\circ} = \text{_____} \text{ cal/}^{\circ}\text{K-gfw} \text{ for _____} \leq T \leq \text{_____}$			
$C_p^{\circ} = \text{_____} \text{ cal/}^{\circ}\text{K-gfw} \text{ for _____} \leq T \leq \text{_____}$			
$C_p^{\circ} = \text{_____} \text{ cal/}^{\circ}\text{K-gfw} \text{ for _____} \leq T \leq \text{_____}$			
METHOD OF SELECTING DATA:			
$C_{p1}^{\circ}$			
$C_{p2}^{\circ}$			
$C_{p3}^{\circ}$			

Figure 7 COMPILATION SHEET NO. 5

COMPILATION SHEET NO. 6  
REFERENCES

NO.	
1	
2	
3	
4	
5	
6	
7	
8	
9	
10	
11	
12	
13	
14	
15	
16	
17	
18	
19	

Figure 8    COMPILATION SHEET NO. 6



as an equation, but as tabular data, then the list of  $C_p^\circ$  values at corresponding temperatures must be tabulated. Similarly, on Compilation Sheet No. 4 (figure 6), if heat-content values are the experimental quantity measured, rather than heat capacity, then this should be shown on this sheet. The purpose of showing two references (secondary and original) is to delineate the source of data. Thus, if a certain author quotes another's value, the first author would be considered as a secondary reference. Compilation Sheet No. 6 (figure 8) provides a bibliography for the compound being considered.

## 5. Possibility of Mechanized Bibliography

It is recognized that the bibliography and property file as shown in sections VIII and IX (Volume 2) have certain limitations. One of these limitations rests in the fact that one must refer to the property file and then manually find the selected references in the bibliography (section VIII). In view of the fact that the bibliography is compiled on IBM punched cards, it might appear appropriate to use computer techniques to compile selected bibliographies for any compound of interest. Hence, a bibliography for a given compound could be compiled directly from the IBM cards. The separate steps now required could be eliminated. Although some consideration was given to the possibility of such a machine compilation of specialized bibliographies, it was not found practical with time limitations to carry this idea to completion. However, preliminary consideration indicated that the method would be feasible.

### C. CHOICE OF PHYSICAL CONSTANTS

In a project of this nature, it is necessary that a uniform set of physical constants be adopted. The earlier work which had been initiated in May 1960 had adopted a particular set of constants as indicated in the final report by Barriault *et al.*<sup>1</sup> To maintain consistency with the earlier work, the same set of physical constants has been used in the present work. Thus, the basic constants have been taken from the work of Cohen, Crowe, and Dumond.<sup>2</sup> After conversion of the physical atomic weight-scale values listed by Cohen *et al.*<sup>2</sup> to the chemical atomic scale, using the conversion factor (1.000275) from Birge,<sup>3</sup> the following values have been obtained:

Gas constant  $R = 1.98726 \text{ cal deg K}^{-1} \text{ mole}^{-1}$ ,

Avogadro's number  $N = (6.02320 \pm 0.00016) \times 10^{23}$ ,

1 thermochemical calorie = 4.1840 absolute joules.

These constants and others as given in the report by Barriault *et al.*<sup>1</sup> have been retained. The chemical atomic weight scale given by Wichers<sup>4</sup> has also been used in this work.

It should be pointed out that several improvements were made in the physical constant situation recently. In 1961, a unified physical-chemical atomic weight scale was adopted by IUPAC,<sup>5-9</sup> wherein  $\text{C}^{12}$  is assigned the mass 12.000. In 1963, further progress was achieved in attaining a universal set of physical constants when the committee on fundamental constants of the National Academy of Sciences National Research Council<sup>10</sup> adopted a list of best values. Some of the values obtained in this new work are

$R = 8.3143 \text{ joule deg K}^{-1} \text{ mole}^{-1} = 1.9872 \text{ cal deg K}^{-1} \text{ mole}^{-1}$ ,

$N = 6.02252 \times 10^{23}$ ,

1 thermochem. cal. = 4.1840 absolute joules.

It may be seen that these newer values have changed only slightly from the values utilized in the work of this project, and the effects on the thermodynamic functions will be very small.

With the recent adoption of the new sets of constants, it would be desirable that any new compilation projects should utilize such values. However in the present work, this was not possible since the values were still in a state of flux; and further, because the work had already been initiated with a given set of constants which was the most up to date at the start of the project.

## REFERENCES FOR SECTION IIC

1. Barriault, R. J. et al, ASD TR 61-260, Pt. I, Vol. 1 (May 1962), p. 1-22.
2. Cohen, E. R., K. M. Crowe, and J. W. M. Dumond, Fundamental Constants of Physics, Interscience, New York (1957).
3. Birge, R. T., Rept. Prog. Phys. 8, 90 (1942).
4. Wichers, E., J. Am. Chem. Soc. 80, 4121 (1958).
5. Anon., IUPAC (International Union of Pure and Applied Chemistry) revises atomic weight values, Chem. Eng. News 39, 42-43 (20 November 1961); C. A. 56, 4110i (1962).
6. Remy, H., Standardization of atomic weights and a new atomic weight table, Naturwiss. 49, 289 (1962); C. A. 57, 6627 (1962).
7. Remy, H., [The] New atomic-weight basis, its foundation and its effects, Chem. Z. 86, 167 (1962); C. A. 57, 6627 (1962).
8. Labbauf, A., Carbon-12 scale of atomic masses, J. Chem. Educ. 39, 282 (1962).
9. Wichers, A., New scale of nuclidic masses and atomic weights, Nature 194, 621 (1962).
10. Anon., Consistent set of physical constants proposed by Committee on Fundamental Constants of the National Academy of Sciences National Research Council, Chem. Eng. News 41, 43-44 (18 November 1963).

## D. THERMODYNAMIC TABLE FORMAT

The thermodynamic table format utilized in this report is amply illustrated by the tables in section VII (Volume 2 ). This format follows closely the pattern of earlier work on this project and also the JANAF tables.

### 1. Consistency of Avco RAD Tables with JANAF Format

A further attempt has been made to remain consistent with the JANAF format by including a data summary on the back of each table. To aid in maintaining consistency of format for these thermodynamic data summaries, basic format sheets patterned after the JANAF example have been prepared. Samples of these format sheets are shown in figures 9 to 13. Some minor changes from the JANAF example include provisions for uncertainty estimates and a separate tabulation of references.

There are two differences between the JANAF and Avco RAD tables as follows:

- a. The present Avco RAD tables are prepared so that double entries are provided at any temperature for which a discontinuity exists in the thermal functions.
- b. In the case of condensed phases, Avco RAD prepares a single table of solid and melted phases corresponding to regions of thermal stability, whereas JANAF prepares two tables, both of which are extrapolated into regions of instability.

### 2. Compatibility of Avco RAD Tables with JANAF Tables

To ensure that the tables generated on this project be as compatible as possible with the JANAF tables, a meeting was held with Dr. D. R. Stull, editor of the JANAF tables, early in this project.

Various aspects were considered, in particular, the problems of (a) fundamental physical constants, (b) differences in computational techniques, and (c) different evaluations of basic experimental data; thus, leading to a different choice of reference state.

The use of very slightly different physical constants by the Avco RAD and JANAF tabulations was discussed, and it was mutually felt that what differences did exist between the JANAF and Avco RAD tabulations were insignificant as far as they affected the tables. In regard to the new molecular weight scale adopted in August 1961, Stull stated that JANAF was still using the old chemical scale of molecular weights and would probably continue doing so until at least the end of 1962. When the new

\_\_\_\_\_ (Name) \_\_\_\_\_ (Formula) (REFERENCE STATE) gfw = \_\_\_\_\_  
 \_\_\_\_\_ 0 °K to \_\_\_\_\_ °K Crystal  
 \_\_\_\_\_ °K to \_\_\_\_\_ °K Liquid  
 \_\_\_\_\_ °K to \_\_\_\_\_ °K Ideal Monatomic Gas  
 $\Delta H_{f0}^{\circ} = 0$   $\Delta H_{f298.15}^{\circ} = 0$   
 $\Delta H_{s298.15}^{\circ} =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  $S_{298.15}^{\circ} =$  \_\_\_\_\_ cal.deg<sup>-1</sup>.gfw<sup>-1</sup>  
 $T_i =$  \_\_\_\_\_ °K  $\Delta H_i =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 $T_m =$  \_\_\_\_\_ °K  $\Delta H_m =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 $T_b =$  \_\_\_\_\_ °K  $\Delta H_v =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 $H_{298.15}^{\circ} - H_0^{\circ} =$  \_\_\_\_\_ cal.gfw<sup>-1</sup>  
 $C_p^{\circ} =$  \_\_\_\_\_ l.deg<sup>-1</sup>.gfw<sup>-1</sup> \_\_\_\_\_ °K ≤ T ≤ \_\_\_\_\_ °K

\_\_\_\_\_  
 (Statement of Structure)

\_\_\_\_\_  
 Heat of Formation

\_\_\_\_\_  
 Heat Capacity and Entropy

\_\_\_\_\_  
 Melting

\_\_\_\_\_  
 Vaporization

\_\_\_\_\_  
 References

Summary of Uncertainty Estimates (Optional: if data avail.)

T, °K	cal/°K gfw			Kcal/gfw			log K <sub>p</sub>
	C <sub>p</sub> <sup>°</sup>	S <sub>T</sub> <sup>°</sup>	-(F <sub>T</sub> <sup>°</sup> - H <sub>298</sub> <sup>°</sup> )/T	H <sub>T</sub> <sup>°</sup> - H <sub>298</sub> <sup>°</sup>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	

Figure 9 BASIC DATA FORMAT FOR REFERENCE STATE ELEMENTS

\_\_\_\_\_ (Name) \_\_\_\_\_ (Formula) (CONDENSED PHASE) gfw = \_\_\_\_\_  
 $\Delta H_{298.15}^{\circ} =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  $S_{298.15}^{\circ} =$  \_\_\_\_\_ cal.deg.<sup>-1</sup>.gfw<sup>-1</sup>  
 $T_f =$  \_\_\_\_\_ °K  $\Delta H_f =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 $T_m =$  \_\_\_\_\_ °K  $\Delta H_m =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 $H_{298.15}^{\circ} - H_0^{\circ} =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 $C_p^{\circ} =$  \_\_\_\_\_ cal.deg.<sup>-1</sup>.gfw<sup>-1</sup> \_\_\_\_\_ °K ≤ T ≤ \_\_\_\_\_ °K

\_\_\_\_\_  
 (Statement of Structure)

Heat of Formation

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Heat Capacity and Entropy

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Melting and Vaporization

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

References

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Summary of Uncertainty Estimates (Optional: if data avail.)

T, °K	cal/°K gfw			Kcal/gfw			log K <sub>p</sub>
	C <sub>p</sub> <sup>°</sup>	S <sub>T</sub> <sup>°</sup>	-(F <sub>T</sub> <sup>°</sup> - H <sub>298</sub> <sup>°</sup> )/T	H <sub>T</sub> <sup>°</sup> - H <sub>298</sub> <sup>°</sup>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	

Figure 10 BASIC DATA FORMAT FOR CONDENSED PHASE COMPOUNDS

\_\_\_\_\_ ( \_\_\_\_\_ ) (IDEAL GAS) gfw = \_\_\_\_\_  
 (Name) (Formula)  
 $\Delta H_{f0}^{\circ} = \text{_____ Kcal.gfw}^{-1}$   $\Delta H_{f298.15}^{\circ} = \text{_____ Kcal.gfw}^{-1}$   
 Ground State Configuration \_\_\_\_\_  $S_{298.15}^{\circ} = \text{_____ cal.deg}^{-1}.\text{gfw}^{-1}$   
 $H_{298.15}^{\circ} - H_0^{\circ} = \text{_____ Kcal.gfw}^{-1}$

Electronic levels and multiplicities

\_\_\_\_\_  
 (Statement of Source of data)  
 \_\_\_\_\_  
 \_\_\_\_\_

Heat of Formation

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Heat Capacity and Entropy

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

References

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Summary of Uncertainty Estimates (Optional: if data avail.)

T, °K	cal/°K gfw			Kcal/gfw			log K <sub>p</sub>
	C <sub>p</sub> <sup>o</sup>	S <sub>T</sub> <sup>o</sup>	-(F <sub>T</sub> <sup>o</sup> - H <sub>298</sub> <sup>o</sup> )/T	H <sub>T</sub> <sup>o</sup> - H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	

Figure 11 BASIC DATA FORMAT FOR MONATOMIC GASES

\_\_\_\_\_ ( \_\_\_\_\_ )  
 (Name) (Formula) (IDEAL GAS) gfw = \_\_\_\_\_  
 $\Delta H_{f0}^\circ = \text{_____ Kcal.gfw}^{-1}$   $\Delta H_{f298.15}^\circ = \text{_____ Kcal.gfw}^{-1}$   
 Ground State Configuration \_\_\_\_\_  $S_{298.15}^\circ = \text{_____ cal.deg}^{-1}.\text{gfw}^{-1}$   
 $H_{298.15}^\circ - H_0^\circ = \text{_____ Kcal.gfw}^{-1}$

cm <sup>-1</sup>									
State	g	E	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$B_e$	$a_e$	$\gamma_e \times 10^5$	$D_e \times 10^6$

#### Heat of Formation

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

#### Heat Capacity and Entropy

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

#### References

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Summary of Uncertainty Estimates (Optional: if data avail.)

T, °K	cal/°K gfw			Kcal/gfw			log K <sub>p</sub>
	C <sub>p</sub> <sup>°</sup>	S <sub>T</sub> <sup>°</sup>	-(F <sub>T</sub> <sup>°</sup> - H <sub>298</sub> <sup>°</sup> )/T	H <sub>T</sub> - H <sub>298</sub>	ΔH <sub>f</sub> <sup>°</sup>	ΔF <sub>f</sub> <sup>°</sup>	

Figure 12 BASIC DATA FORMAT FOR DIATOMIC MOLECULAR GASES



\_\_\_\_\_ ( \_\_\_\_\_ ) (IDEAL GAS) gfw = \_\_\_\_\_  
 (Name) (Formula)  
 $\Delta H_f^\circ =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  $\Delta H_f^\circ_{298.15} =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>  
 Point Group \_\_\_\_\_  $S^\circ_{298.15} =$  \_\_\_\_\_ cal.deg<sup>-1</sup>gfw<sup>-1</sup>  
 $H^\circ_{298.15} - H^\circ_0 =$  \_\_\_\_\_ Kcal.gfw<sup>-1</sup>

Vibrational levels and multiplicities

$\omega, \text{cm}^{-1}$   $\omega, \text{cm}^{-1}$   
 \_\_\_\_\_ ( ) \_\_\_\_\_ ( ) (Note: multiplicities  
 \_\_\_\_\_ ( ) \_\_\_\_\_ ( ) inserted in ( ))

Bond lengths and angles:

\_\_\_\_\_ distance = \_\_\_\_\_ Å \_\_\_\_\_ distance = \_\_\_\_\_ Å  
 \_\_\_\_\_ Angle = \_\_\_\_\_

Product of moments of inertia:  $I_A I_B I_C =$  \_\_\_\_\_ g<sup>3</sup>.cm<sup>6</sup>  $\sigma =$  \_\_\_\_\_

Heat of Formation

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

Heat Capacity and Entropy

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

References

\_\_\_\_\_  
 \_\_\_\_\_

Summary of Uncertainty Estimates (Optional: if data avail.)

T, °K	- cal/°K gfw			Kcal/gfw			log K <sub>p</sub>
	C <sub>p</sub> <sup>o</sup>	S <sub>T</sub> <sup>o</sup>	-(F <sub>T</sub> <sup>o</sup> - H <sub>298</sub> <sup>o</sup> )/T	H <sub>T</sub> <sup>o</sup> - H <sub>298</sub> <sup>o</sup>	ΔH <sub>f</sub> <sup>o</sup>	ΔF <sub>f</sub> <sup>o</sup>	

Figure 13 BASIC DATA FORMAT FOR POLYATOMIC MOLECULAR GASES

physical constants are officially adopted,\* JANAF will accept the new physical constants and molecular weights simultaneously. At that time, they would reprocess their tables and bring them up to date relative to the new constants. This reprocessing, of course, could not be accomplished immediately and would require a certain interim period of conversion.

Avco RAD has followed a plan similar to that of the JANAF group. That is, the old molecular weight scale has been used, and no changes in physical constants have been made (see section IIC). It should be emphasized that any of the proposed changes in physical constants will have only minor effects on the actual tables.

Some discussion has been devoted to differences in computational techniques. Here again, there do not seem to be any serious differences although another type of inconsistency becomes possible. Both groups use several programs for computation of the same quantity, and thus, it is possible to obtain a different treatment of the data depending on the program. When a given person is preparing a table, a slightly different table could result depending on the choice of handling data. For example, JANAF sometimes calculates all of the properties of a diatomic gas, whereas sometimes it will accept published values of  $C_p^\circ$  for such a gas and compute the other functions. In general, it is clear that small differences could arise from tables prepared in these different ways.

The problem of different evaluations of basic data relevant to a given table has been considered. The most important factor is that involving elements or compounds common to the two tabulations. A list of these is given in table 3.

In table 3, it is seen that 10 elements are common to both projects. A comparison of several of these elements and the respective data obtained by JANAF and Avco RAD has been made. The agreement is quite good. Two examples, which are discussed in more detail below, are oxygen and beryllium.

For the case of the reference state of oxygen (i. e., diatomic oxygen), there are no phase changes, and hence, the greatest discrepancy that can occur results from differences in computational procedures or input data. The data show very good agreement at the lower temperatures with relatively minor changes at the very highest temperature of 6000°K. It is agreed that at the present state of knowledge, neither calculation can be considered right or wrong, and accordingly, the difference between the two tables is not likely to lead to any serious errors.

---

\*The new physical constants were not adopted until late in 1963. See Chem. Eng. News 41, 43 (16 November 1963).

TABLE 3

## LIST OF ELEMENTS BEING STUDIED BY JANAF AND AVCO RAD

Elements for JANAF Only	Elements Common to Both Groups	Elements for Avco RAD Only
Al	B	Ca
Br	Be	Ce
Cl	C	Cr
F	Mg	Dy
H	N	Gd
Hg	O	Hf
I	Si	Ir
K	Ti	La
Li	W	Mn
Na	Zr	Mo
P		Nb
Pb		Nd
S		Os
		Pt
		Re
		Rh
		Sc
		Sm
		Sr
		Ta
		Tc
		U
		V
		Y

The case of the beryllium reference state (which possesses solid, liquid, and gaseous phases) has also been considered since it represents a case having several transitions. JANAF lists a melting point at 1556°K and a boiling point at 2757°K, whereas Avco RAD in a recently revised table of this report gives 1556° and 2768°K, respectively. The agreement is very good. Any experimental determinations of these transition points would undoubtedly be subject to larger errors than the differences shown by either table.

The possibility of mixing Avco RAD and JANAF data for compounds referred to different reference states was also discussed. One might ask, what

would be the effect of using BeCl<sub>2</sub> JANAF data in conjunction with BeO RAD data? Here, the possibility would arise that because of the different boiling points for the reference beryllium state, there might be a small range of temperature where there could be a discontinuity in the thermal functions, such as heat and free energy of formation. The probability of such discrepancies being important would be relatively small because the temperature range involved (from 2757° to 2768°K) was only 11°K.

In summary, it is concluded that there is very good agreement between the JANAF and Avco RAD tabulations. An effort has also been made to reduce further any differences between the tabulations. At the present time, the agreement between tabulations is excellent.

As in any work of this nature, the highest degree of compatibility is best maintained within a single compilation. Therefore, users of tables who wish to combine data from various compilations (JANAF or others) are advised (as has always been necessary heretofore) to refer to the basic data to be sure that no inconsistencies are introduced. It may be mentioned that this applies also within a given compilation. For example, in the first year of this project, a table for hafnium reference state had been issued.<sup>1</sup> Subsequently in the present work, a new table for hafnium reference state has been issued. Since all of the present work (including hafnium compounds) has been based on the present or newer hafnium table, it is likely that an unwary user who utilizes the older hafnium table in combination with the recent tables for hafnium compounds will be introducing inconsistencies. However, all tables from the present report would be expected to be self-consistent. Even here, however, a very careful scientist will read the writeups (section IV) to become more intimately aware of the data used in compiling the present tables.

#### REFERENCE FOR SECTION IID2

1. Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, 2 Vols., ASD TR 61-260, Pt 1 (May 1962).
3. Possibility of Converting Avco RAD Tables to a Reduced Number of Constants

To make the present tables more flexible and available for a greater variety of purposes, some consideration has been given to the possibility of converting the rather bulky tables to a small number of constants. These constants which are the coefficients of equations used to define such functions as heat capacity, entropy, etc., could then be used in electronic computers to regenerate essentially thermodynamic tables when required. By eliminating the necessity for storing large tables and reducing the storage requirements to a few constants per compound, one gains tremendously, particularly in machine calculations of equilibrium compositions

for multicomponent systems. Present-day computers have limited high-speed storage capabilities, and hence, it is desirable to reduce the amount of actual input data.

Wiederkehr<sup>1</sup> and Bowman<sup>2</sup> have illustrated the reduction of JANAF-type tables to seven constants denoted as "m" or "l" values. Thus, heat capacity is evaluated as

$$C_p^\circ = l_1 + l_2T + l_3T^2 + l_4T^3 + l_5T^{-2}$$

Two additional "l" values,  $l_6$  and  $l_7$ , permit calculation of the heat of formation and entropy.

In the present work, it was decided that emphasis should be placed on table preparation. Hence, no effort was made to prepare lists of constants such as the "l" values. However, it was recognized that in future work this would be desirable.

#### REFERENCES FOR SECTION IID3

1. Wiederkehr, R. R. V., Matrix representation of thermodynamic properties of multicomponent systems, J. Chem. Phys. 37, 1192 (1962).
2. Bowman, C. M., A General Method for Calculating the Specific Impulse of High Energy Propellant Mixtures, Rept. AR-35-61, Dow Chem. Co., Midland, Mich. (1 August 1961).
4. Possibility of Mechanized Plotting of Thermodynamic Data

As the current project has developed, more steps have been taken to utilize high-speed-computing machinery. At the present time, it is possible to generate essentially complete output thermodynamic tables on IBM cards, and these cards are now stored for reference purposes.

In view of the availability of these data on IBM cards, it has appeared appropriate to investigate other possible ways of utilizing the data. One possible method of employing these IBM cards is mechanically to plot their values.

Because of the large number of thermodynamic tables, hand plotting would not be practical. However, mechanized plotting may be desirable. If the costs of the operation are reasonable, it may be possible to graph all, or portions, of the data being generated on this project.

At least two advantages can come from graphic figures. For the person who may be preparing the tables, it is possible to make plots and check

for accuracy, etc. That is, the proper trends can be noted. If any erroneous trends are present, they can be much more easily detected from a graph than from a table. On the other hand, often the user may also wish to see a plot of the data rather than extract a number from the tables.

In the light of these facts, it has appeared appropriate to check on the feasibility of the use of mechanized plotting of some typical data generated on this project. For this trial case, the IBM cards containing the data for hafnium dioxide (condensed) ( $\text{HfO}_2$ ) (see table 144 of volume 2) have been used.

To implement the plotting, the IBM cards were first processed on an IBM-1410 digital computer to generate a magnetic tape. This tape was then transferred to a Benson-Lehner Magnetic Tape Converter Model J which fed the Benson-Lehner Electroplotter Model J.

The latter device is capable of plotting 300 points per minute. The final graphs obtained are used directly in this report. Notations have been added to maintain uniformity with other graphs, but the actual plots have not been touched. It is possible that even the notations can be placed on the graphs directly by the electroplotter in the future.

Various types of operating conditions are utilized in figures 14 to 20 to illustrate the results of the mechanized plotting. However, each of the figures corresponds to a different type of data.

Thus, figure 14 is a plot of  $C_p^\circ$  data for  $\text{HfO}_2$  versus temperature. In figure 15, values of entropy are plotted. Free-energy functions are plotted in figure 16. Enthalpy contents are plotted in figure 17. The variation of the heat of formation with temperature is shown in figure 18. In figure 19, a plot of the free energy of formation of  $\text{HfO}_2$  versus temperature is shown. Finally, figure 20 presents a plot of  $\log_{10} K_p$  versus temperature.

The graphs in figures 14 to 20 have been prepared using different methods of plotting. Thus in figures 14 to 16, continuous lines are

used to plot the data for  $C_p^\circ$ ,  $S_T^\circ$ , and  $-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$  on a background with

no grids. Continuous lines are used to plot  $H_T^\circ - H_{298}^\circ$ ,  $\Delta H^\circ$ , and  $\Delta F^\circ$  versus  $T$  on a background containing grids in figures 17 to 19. Finally, figure 20 shows a case where the actual tabulated points are plotted on a background with no grids but with no effort to generate a smooth line as in the earlier cases.

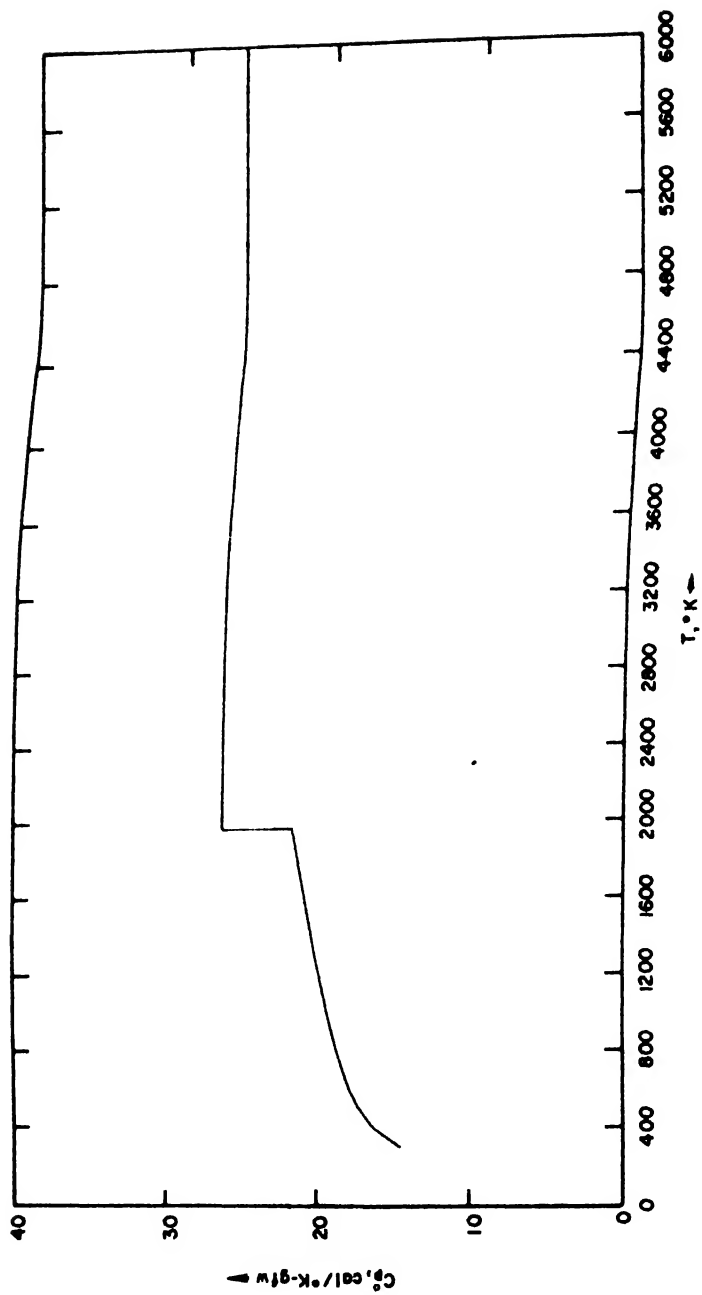


Figure 14 MACHINE PLOT OF  $C_p$  DATA FOR  $H_2O_2$ (<sub>cond</sub>)  
VERSUS TEMPERATURE

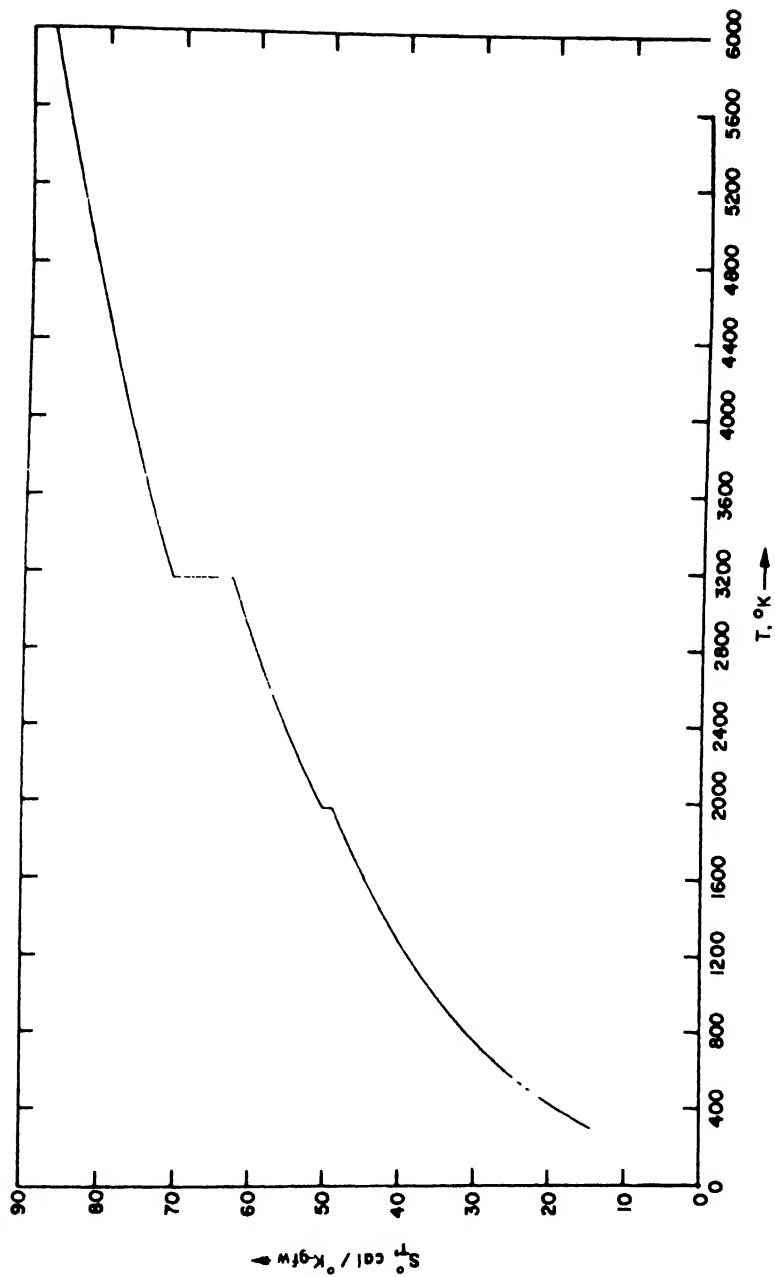


Figure 15 MACHINE PLOT OF ENTROPY DATA FOR  $\text{HIO}_2(\text{cond})$   
VERSUS TEMPERATURE



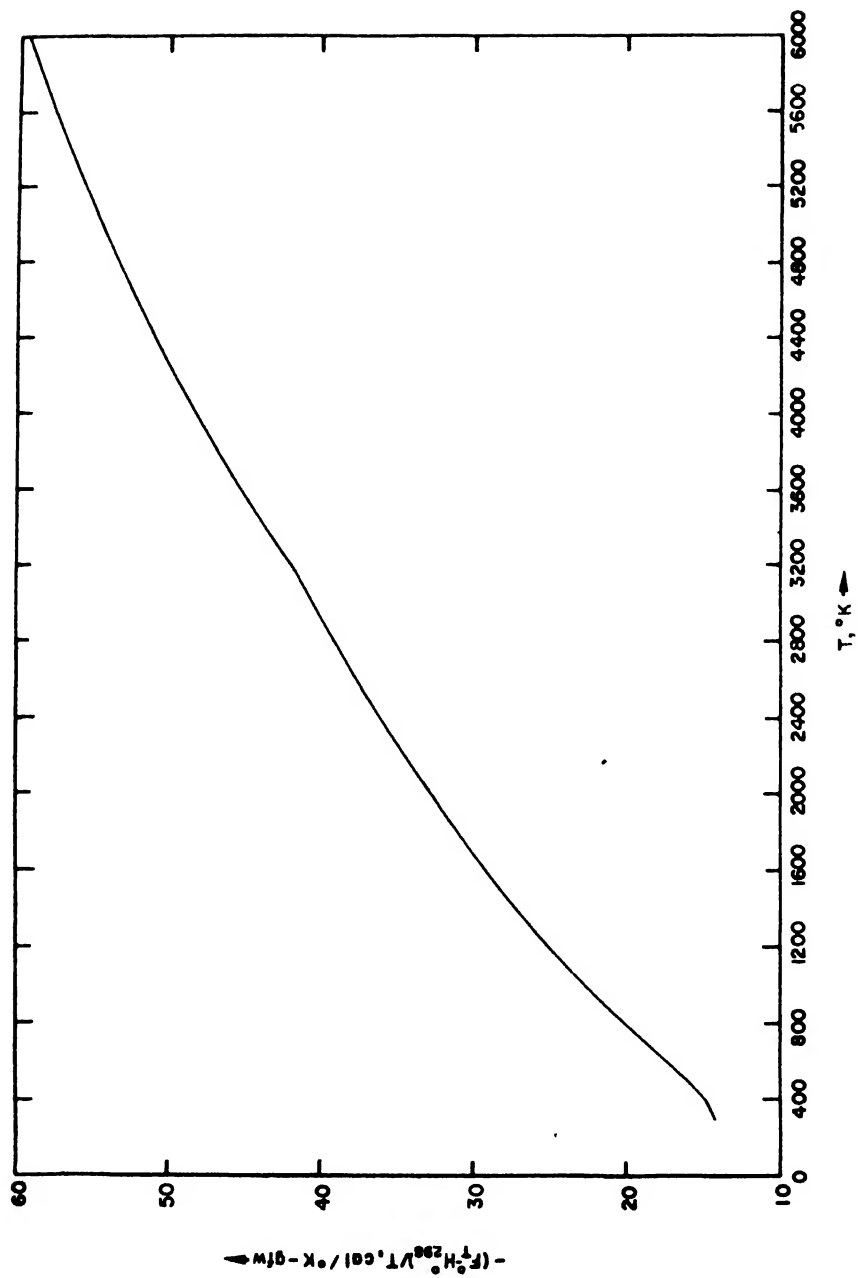


Figure 16 MACHINE PLOT OF FREE - ENERGY FUNCTIONS FOR  $\text{HfO}_2(\text{cond})$  VERSUS TEMPERATURE

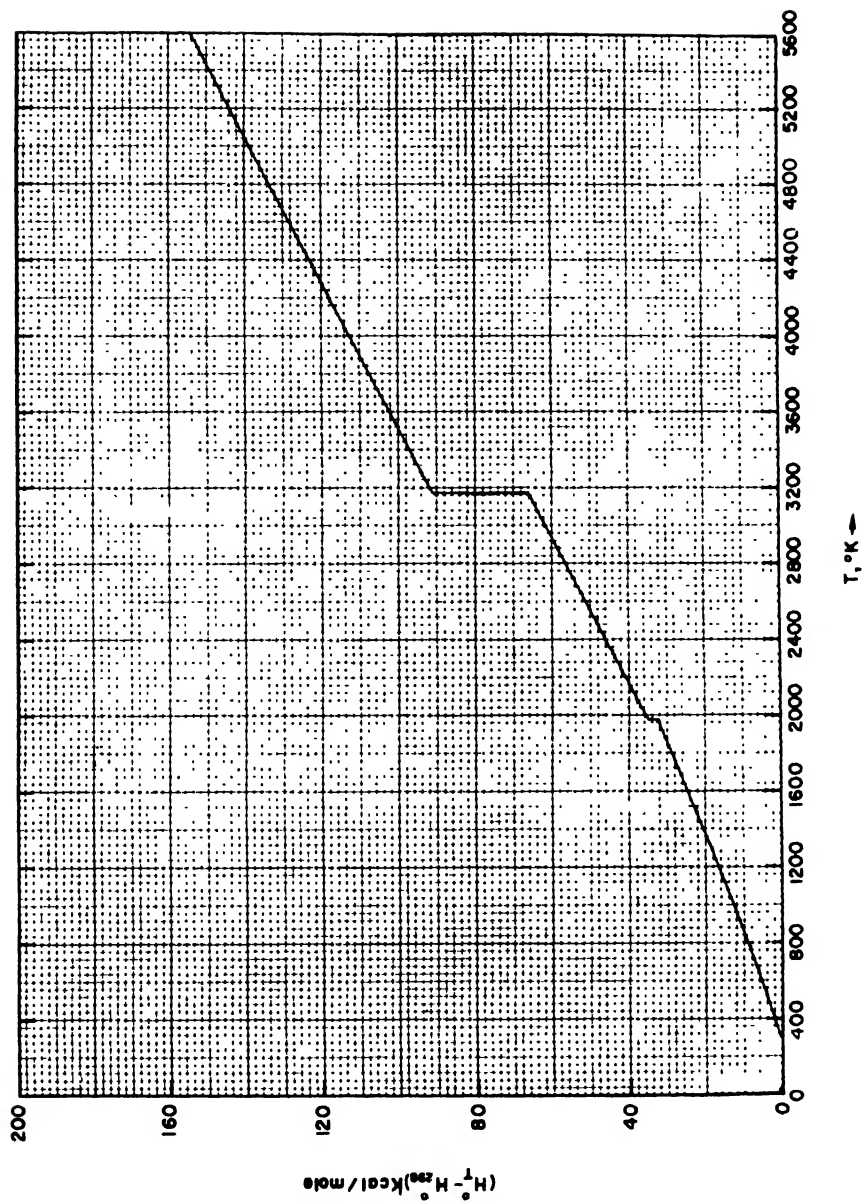


Figure 17 MACHINE PLOT OF ENTHALPY CONTENT FOR  $\text{HfO}_2(\text{cond})$  VERSUS TEMPERATURE

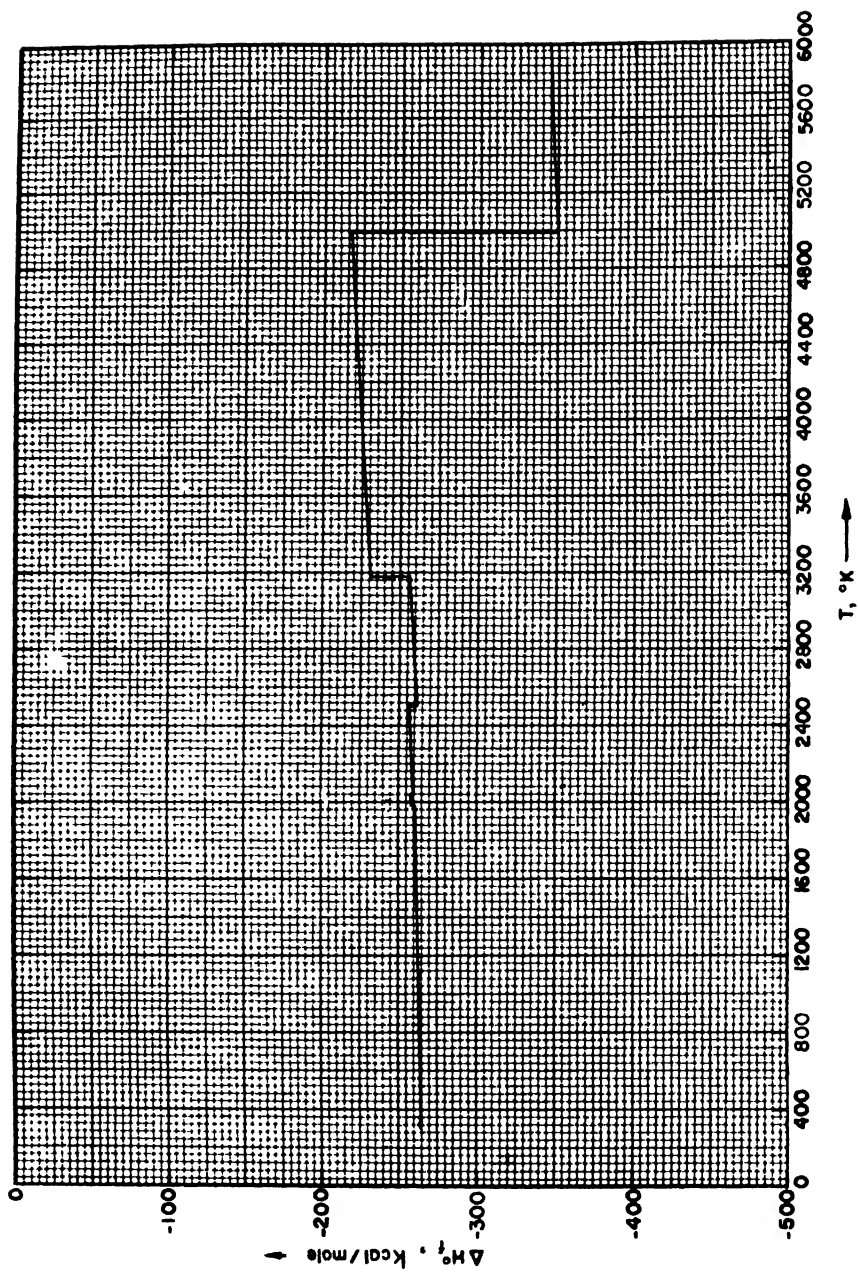


Figure 18 MACHINE PLOT OF HEAT OF FORMATION FOR  $\text{HfO}_2(\text{cand})$   
VERSUS TEMPERATURE

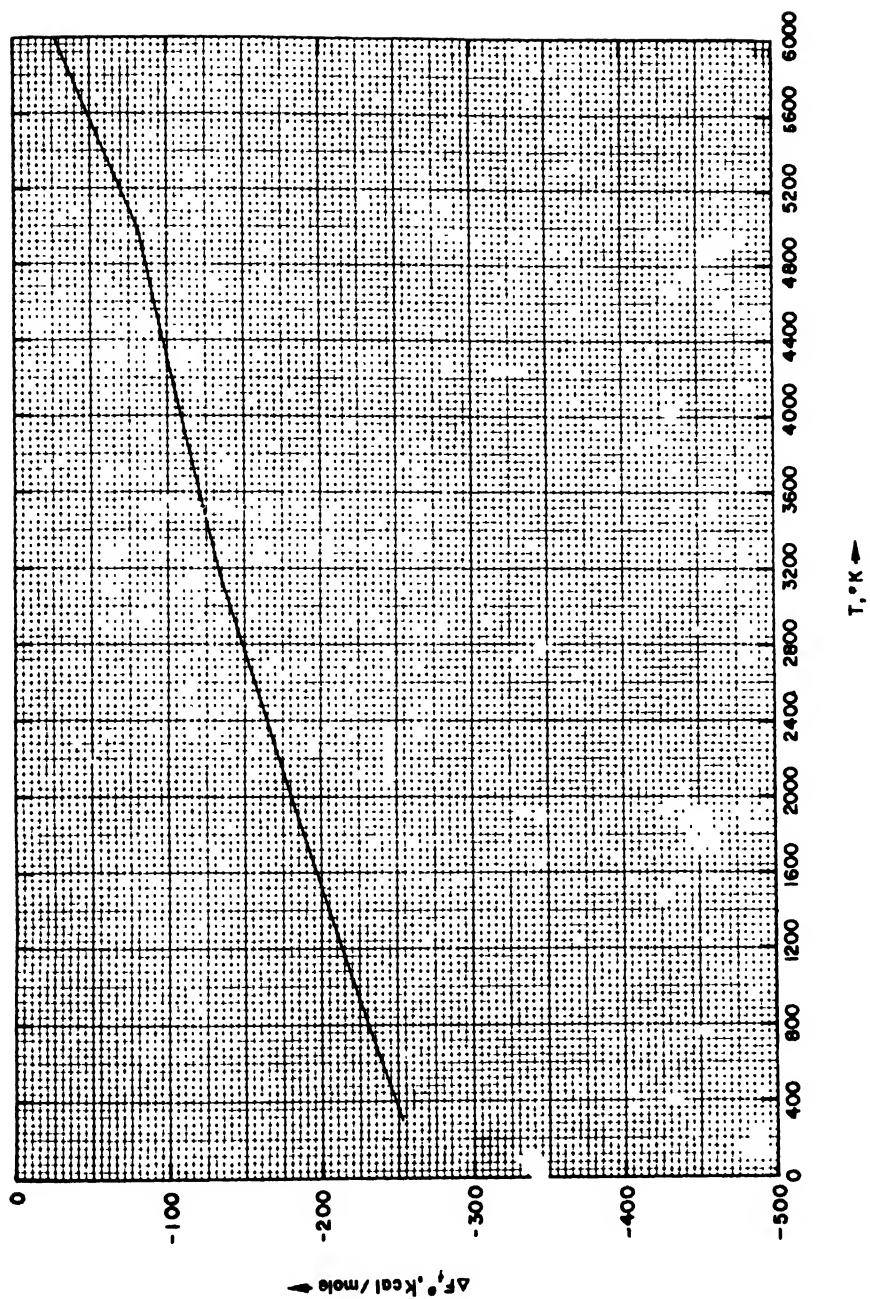


Figure 19 MACHINE PLOT OF FREE ENERGY OF FORMATION FOR  $\text{H}_2\text{O}_2(\text{cond})$  VERSUS TEMPERATURE

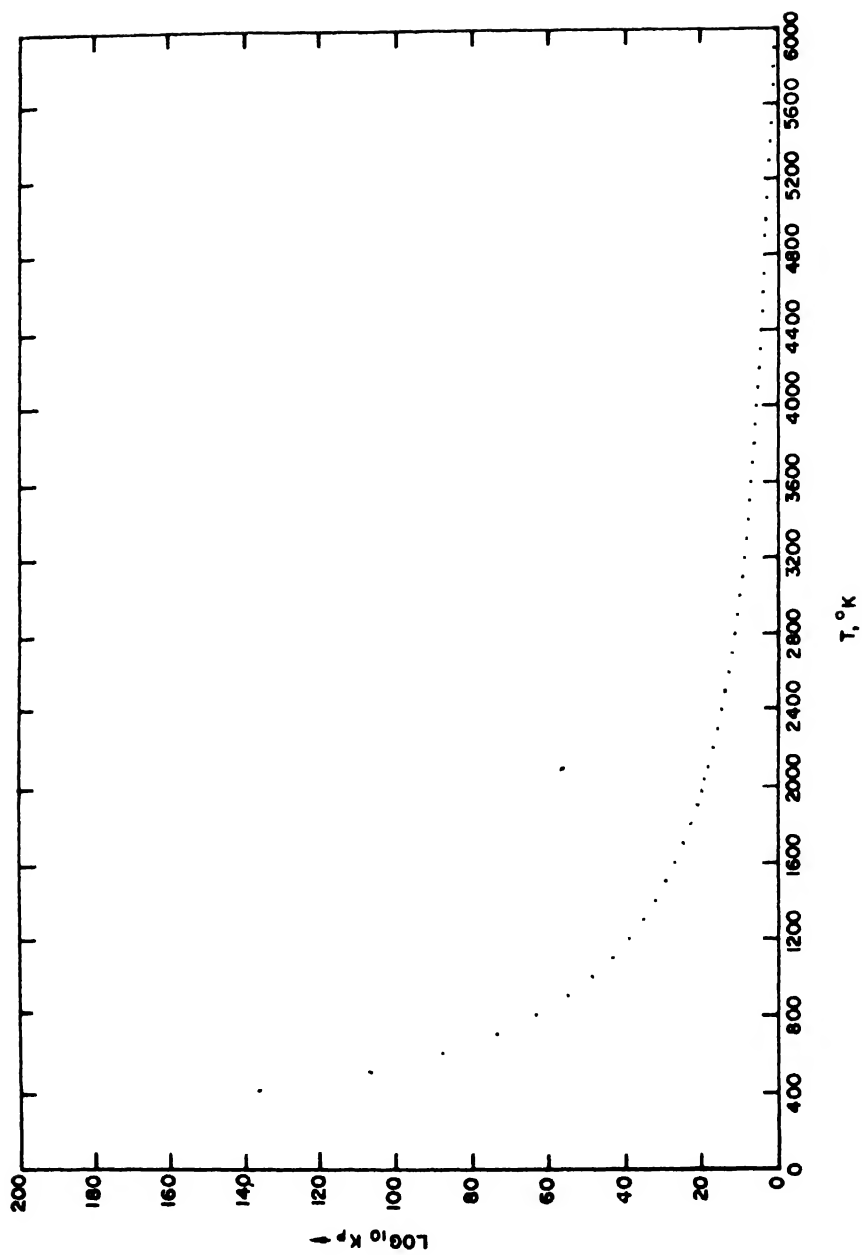


Figure 20 MACHINE PLOT OF  $\log_{10} K_p$  FOR  $\text{HfO}_2(\text{cond})$  VERSUS TEMPERATURE

The plotted data presented in figures 14 to 20 illustrate the techniques developed with a minimum of effort. It is possible that improvements could also be achieved. Plans to extend this technique are being held in abeyance pending feedback from the scientific community as to its desirability. Again, it should be emphasized that the present trial is a purely experimental one to present the potentialities of machine plotting.

### III. COMPUTATIONAL METHODS AND NUMERICAL RESULTS OF GENERAL INTEREST

#### A. COMPUTER PROGRAMS

##### 1. General

During the present project, much computational work has been performed with the aid of electronic computers. Initial phases of this project had the aid of a Philco-S2000 computer and subsequently an IBM-7094. Computer programs were developed which can aid in producing the following five basic types of table:

- a. Monatomic Gas Tables,
- b. Diatomic Gas Tables,
- c. Polyatomic Gas Tables,
- d. Condensed Phase Tables, and
- e. Reference Tables.

At the beginning of this present project, all of the existing computer programs were independent of each other without standard output formats. Hence in the present work, the various computer programs (i. e., monatomic, diatomic, etc.) were modified so as to yield output in the same form as the tables published in this work. Also, some of the input to certain programs were modified to accept IBM data cards directly. Thus, decks of IBM cards representing a particular compound could be used directly without further data handling.

Additional consideration has been given to increasing the ease of data handling and to reduce the chance for human error in computer operations. It is desirable to store any required data on magnetic tape and call for the data automatically when computations are needed. Such procedures should increase the reliability of tables and also increase the rate of table production. As yet, this goal has not been achieved.

In addition to the steps taken to make the computer programs more automatic, several new programs were developed. Thus, a smoothing program was formulated which "smooths" raw experimental data. A "least-squares-fit program" was utilized to fit data to simple expressions often used to express heat-capacity data. For example, input  $C_p^\circ$  data could be fitted to various analytical equations. A "Shomate program" was developed

to fit experimental enthalpy data to an analytical equation. The general method had been described by Shomate.<sup>1</sup> A program was also developed to compute the heat of reaction at 298.15°K when experimental vapor pressures at higher temperatures were given. Another program variation permitted Lagrangian interpolation in thermodynamic tables of the type generated on this project. Another program used for more complex equilibria was the thermochemical equilibrium program developed in other projects at Avco RAD. This program utilized magnetic tape to store all pertinent data. A minimum of auxiliary input data to specify the problem of interest, then, would permit calculations involving a maximum of 200 species to be performed. The equilibrium partial pressures or concentration of all species could be computed for a given temperature or pressure.

Further comments on the methods for calculation of particular tables follow.

## 2. Monatomic Gas Tables

The equations used to compute a monatomic gas table have been given on pages 1-41 to 1-47 of the final report<sup>2</sup> on the earlier phase of this project.

## 3. Diatomic Gas Tables

The equations which have formed the basis for computation of diatomic gas tables are given on pages 1-48 to 1-55 of the earlier final report.<sup>2</sup> The equations permit consideration of multiple electronic states and various spectroscopic constants. These include the following:

$\omega_e$  = vibrational frequency,

$\omega_e x_e$  = anharmonicity constant,

$\omega_e y_e$  = higher-order anharmonicity constant,

$B_e$  = rotational constant for the equilibrium separation of atoms,

$\alpha_e$  = vibrational-rotational coupling constant,

$\gamma_e$  = higher-order term to correct the rotational constant  $B_e$ , and

$D_e$  = stretching constant which considers the effect of centrifugal force.

## 4. Polyatomic Gas Tables

Calculations of properties of polyatomic gases were made using the equations given on pages 1-56 to 1-61 of the earlier final report.<sup>2</sup> Two aspects



of this calculation were recognized; i. e. , linear and nonlinear molecules. In the calculations, all interaction terms were neglected; i. e. , it was assumed that the partition function could be factored into a product of several individual terms containing a single variable.

During the present work, modification was made in the polyatomic gas program so that the product of the three principal moments of inertia,  $I_A I_B I_C$ , could be calculated from the cartesian coordinates given as input data for the given molecule.

## 5. Condensed Phase Tables

On pages 1-62 to 1-66 of the previous report<sup>2</sup> are given details of the calculation of a condensed phase table. Two general methods of calculation have been used to obtain thermodynamic functions for condensed phases. In the first method, an analytical expression of the form  $C_p^\circ = A + BT + CT^{-2} + DT^2$  is used. In the second method, experimental  $C_p$  data given at various temperatures are integrated by an iterative technique to yield the thermodynamic table at the prescribed temperatures. In the present work, the first method has been used to a greater extent because of the greater availability of data in analytical form and because of the greater ease of performing such calculations.

## 6. Reference Tables

In general, reference tables are more time-consuming to prepare than others. Usually one must first obtain thermodynamic functions [i. e. ,  $C_p^\circ$ ,  $S_T^\circ$ ,  $-(F_T^\circ - H_{298}^\circ)/T$ ,  $(H_T^\circ - H_{298}^\circ)$ ] for both the condensed phase and the monatomic gas. Then, original vapor-pressure data must be analyzed using the above free-energy functions to calculate the heat of sublimation into the monatomic gas. Next, the boiling temperature can be calculated. Here, it may be noted that the phrase "boiling temperature" is used to indicate the temperature at which the pressure of monatomic gas reaches 1 atm. In the event that diatomic or polyatomic gaseous species are important, the true boiling point will be somewhat lower than the calculated boiling point. However for all elements considered in the present work, it is believed that the calculated boiling point is essentially equivalent to the true boiling point because of the absence of diatomic and higher species. In cases such as carbon, nitrogen, and oxygen which form polyatomic or diatomic gaseous species, no boiling point has been calculated, so that the above remarks are not applicable.

### REFERENCES FOR SECTION IIIA

1. Shomate, C. , [A] Method for evaluating and correlating thermodynamic data, J. Phys. Chem. 58, 368 (1954).
2. Barriault, R. J. , et al, ASD TR 61-260, Pt I. , Vol. I (May 1962).

## B. ESTIMATION OF FUNDAMENTAL VIBRATION FREQUENCIES AND INTERNUCLEAR DISTANCES FOR POLYATOMIC AND DIATOMIC GASES

A number of equations which occur frequently in discussions of fundamental vibration frequencies of gaseous metal oxides are summarized immediately below for convenience in future reference. Although the discussions are applied to metal oxides, they could be equally well applied to other compounds, such as carbides, borides, and nitrides.

### 1. Metal Monoxides

Steele and Lippincott<sup>1</sup> have suggested a method for the construction of reliable internuclear potential curves of the form

$$V = D_e \left\{ 1 - \exp \left[ -n \Delta r^2 / 2r \right] \right\} \left\{ 1 + a f(r) \right\}, \quad (\text{IIIB1-1})^*$$

from a knowledge of  $\omega_e$  and  $r_e$  alone.  $n$  is defined as in equation (IIIB1-2), and  $k_e$  is the force constant referred to zero displacement.

$$n = k_e r_e / D_e. \quad (\text{IIIB1-2})$$

The parameter "a" in equation (IIIB1-1) was found to be related to the position of the elements in the periodic table when referring to the ground state of diatomic molecules. This "periodicity" in "a" was shown to lead to relationships from which  $D_e$ ,  $a_e$ , and  $r_e \omega_e$  can also be calculated for any nonionic excited state from  $\omega_e$  and  $r_e$  alone. It was found that  $\omega_e r_e^2$  is not constant for all states of any molecule but is dependent in a predictable manner on the other spectroscopic constants.

The relations given by Steele and Lippincott<sup>1</sup> for calculating  $D_e$ ,  $a_e$  and  $r_e \omega_e$  with a suitable form of  $f(r)$  are

$$D_e = \left( \frac{1}{2} \right) b^2 k_e r_e^2 (1 - 5a/4)^2, \quad (\text{IIIB1-3})$$

$$b = 1.065, \quad (\text{IIIB1-4})$$

$$G = 8(1 + F)^2, \quad (\text{IIIB1-5})$$

---

\*  $\Delta r = r - r_e$ ,

where  $r$  = bond distance, and  
 $r_e$  = equilibrium bond distance.

$$a = F(1 + 5F/4)^{-1} \quad , \quad (\text{IIIB1-6})$$

$$G = 8x_e\omega_e/B_e \quad , \quad (\text{IIIB1-7})$$

$$F = a_e\omega_e/6B_e^2 \quad . \quad (\text{IIIB1-8})$$

The relation given for predicting the value of "a" for the ground state of a homonuclear molecule from the location of the element in the periodic table is

$$a = 0.335 + 0.080 \delta + 0.02 (n_c + n_r) \quad , \quad (\text{IIIB1-9})$$

where  $\delta$  is equal to unity for all elements except hydrogen, and  $n_c$  and  $n_r$  are the column and row numbers of the element in the periodic table, respectively. For heteronuclear molecules, "a" was reported to be given satisfactorily by the mean value of the "a" for the homonuclear diatomic molecules of the constituent atoms.

The relation given by Steele and Lippincott<sup>1</sup> for calculating  $D_e$ ; i. e. , equation (IIIB1-3), is expected to be more accurate than the Morse relation; i. e. ,

$$D_e = \frac{\omega_e^2}{4\omega_e x_e} \quad . \quad (\text{IIIB1-10})$$

It should be pointed out that Steele and Lippincott<sup>1</sup> have noted that their relationship for  $D_e$  is valid for all diatomic molecules in their ground states except those involving transition atoms. Since the present work is concerned to a major extent with transition atoms, the relations given above by Steele and Lippincott have been of limited value. They are shown here primarily for illustrative purposes.

In the work for this project, usually experimental determinations of the internuclear distance  $r_e$  and the vibrational frequency  $\omega_e$  have been available and were used in the calculations. Heats of dissociation were derived from experimental vaporization studies whenever available. Whenever it was necessary to estimate internuclear distances or vibrational frequencies, the estimates were made by comparison with related molecules. Individual cases should be consulted for exact details.

#### REFERENCE FOR SECTION IIIB1

1. Steele, D. and E. R. Lippincott, J. Chem. Phys. 35, 2065 (1961).

## 2. Linear Metal Dioxides (MO<sub>2</sub>)

The estimation of the fundamental frequencies of linear MO<sub>2</sub> molecules was based on the following three assumptions:

a. The fundamental vibrations may be described by a valence force-field method.<sup>1</sup>

b. The stretching force constant ( $k_1$ ) for the MO<sub>2</sub> molecule is the same as that for the corresponding MO molecule. The latter assumption has been employed by previous workers.<sup>2,3</sup> The stretching force constant for the MO molecule was, therefore, calculated by means of equation (IIIB2-1),

$$k_1 = 4\pi^2 c^2 \mu \omega_e^2 \quad (\text{IIIB2-1})$$

where  $c$  is the velocity of light,  $\mu$  is the reduced mass of the MO molecule, and  $\omega_e$  is the fundamental frequency (cm<sup>-1</sup>).

c. The ratio of the bond-bending ( $k_\delta/l^2$ , where  $l$  is the internuclear distance) and bond-stretching force constants was taken as 0.0340, the average of those observed for several linear molecules.<sup>1</sup>

$$\frac{\left(\frac{k_\delta}{l^2}\right)}{k_1} = 0.0340. \quad (\text{IIIB2-2})$$

The values of the fundamental frequencies ( $\omega_1$ , doubly degenerate  $\omega_2$ , and  $\omega_3$ ) were then calculated from the following equations:

$$\omega_1^2 = \left[ \frac{1}{0.3548 \times 10^{23}} \right] \left( \frac{k_1}{M_O} \right) \quad (\text{IIIB2-3})$$

$$\omega_2^2 = \frac{\left(\frac{2}{M_O}\right) \left[ 1 + 2 \left(\frac{M_O}{M_M}\right) \right] \left(\frac{k_\delta}{l^2}\right)}{0.3548 \times 10^{23}}, \quad (\text{IIIB2-4})$$

$$\omega_3^2 = \frac{\left[ 1 + 2 \left(\frac{M_O}{M_M}\right) \right] \left(\frac{k_1}{M_O}\right)}{0.3548 \times 10^{23}}. \quad (\text{IIIB2-5})$$

## REFERENCES FOR SECTION IIB2

1. Herzberg, G., Molecular Spectra and Molecular Structure, II. Infra-red and Raman Spectra of Polyatomic Molecules, Van Nostrand, N. Y. (1945).
2. Chandrasekharaiah, M.S. and L. Brewer, U.S. At. Energy Comm. Rept. UCRL-8736 (April 1959).
3. Grimley, R.T., R. P. Burns, and M.G. Inghram, J. Chem. Phys. 34, 664 (1961).

### 3. Nonlinear Metal Dioxides ( $\text{MO}_2$ )

The estimation of the fundamental frequencies of nonlinear MO<sub>2</sub> molecules was based on the following three assumptions:

- a. Assumptions (2a) and (2b) on the preceding page, used for linear  $\text{MO}_2$  molecules.
- b. The ratio of the bond-bending and bond-stretching force constants is 0.940, the average of those observed for several nonlinear molecules<sup>1</sup>; i.e.,

$$\frac{\left(\frac{k_{\delta}}{l^2}\right)}{k_1} = 0.0940 \quad . \quad (\text{III B } 3-1)$$

The values of the fundamental frequencies ( $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ ) were, therefore, calculated from the following equations:

$$\omega_3^2 = \frac{\left[ 1 + 2 \left( \frac{M_O}{M_M} \right) \sin^2 \alpha \right] \left( \frac{k_1}{M_O} \right)}{0.3548 \times 10^{23}}, \quad (\text{III B 3-2})$$

$$\omega_1^2 + \omega_2^2 = \frac{\left[ 1 + 2 \left( \frac{M_O}{M_M} \right) \cos^2 a \right] \left( \frac{k_1}{M_O} \right) + \left( \frac{2}{M_O} \right) \left[ 1 + 2 \left( \frac{M_O}{M_M} \right) \sin^2 a \right] \left( \frac{k_\delta}{l^2} \right)}{0.3548 \times 10^{23}}, \quad (\text{IIIB 3-3})$$

$$\omega_1^2 \omega_2^2 = \frac{2 \left[ 1 + 2 \left( \frac{M_O}{M_M} \right) \right] \left( \frac{k_1}{M_O^2} \right) \left( \frac{k_\delta}{l^2} \right)}{0.1259 \times 10^{46}} , \quad (\text{IIIB3-4})$$

where

$$a = \frac{\angle O-M-O}{2} . \quad (\text{IIIB3-5})$$

#### REFERENCE FOR SECTION IIIB3

1. Herzberg, G., Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, N.Y. (1945).

#### 4. Planar, Cart-Wheel, Metal Trioxides (MO<sub>3</sub>)

The estimation of the fundamental frequencies of planar, cart-wheel, MO<sub>3</sub> molecules was based on the following three assumptions:

- a. Assumptions (2a) and (2b) previously mentioned, used for linear MO<sub>2</sub> molecules.
- b. The other force constants may be evaluated by averaging the ratios of force constants calculated from observed frequencies for several planar, symmetrical, cart-wheel molecules<sup>1</sup>; i. e.,

$$\frac{\left( \frac{k_\delta}{l^2} \right)}{k_1} = 0.0440 , \quad (\text{IIIB4-1})$$

$$\frac{\left( \frac{k_\Delta}{l^2} \right)}{k_1} = 0.1160 . \quad (\text{IIIB4-2})$$

The values of the fundamental frequencies were, therefore, calculated from the following equations:

$$\omega_1^2 = \left[ \frac{1}{0.3548 \times 10^{23}} \right] \left( \frac{k_1}{M_O} \right) \quad , \quad (\text{IIIB4-3})$$

$$\omega_2^2 = \frac{\left[ 1 + 3 \left( \frac{M_O}{M_M} \right) \right] \left( \frac{1}{M_O} \right) \left( \frac{k_\Delta}{l^2} \right)}{0.3548 \times 10^{23}} \quad , \quad (\text{IIIB4-4})$$

$$\omega_3^2 + \omega_4^2 = \frac{\left[ 1 + \left( \frac{3}{2} \right) \left( \frac{M_O}{M_M} \right) \right] \left[ \left( \frac{k_1}{M_O} \right) + \left( \frac{3}{M_O} \right) \left( \frac{k_\delta}{l^2} \right) \right]}{0.3548 \times 10^{23}} \quad , \quad (\text{IIIB4-5})$$

$$\omega_3^2 \omega_4^2 = \frac{3 \left[ 1 + 3 \left( \frac{M_O}{M_M} \right) \right] \left( \frac{k_1}{M_O^2} \right) \left( \frac{k_\delta}{l^2} \right)}{0.1259 \times 10^{46}} \quad . \quad (\text{IIIB4-6})$$

$\omega_3$  and  $\omega_4$  are both doubly degenerate frequencies.

#### REFERENCE FOR SECTION IIIB4

1. Herzberg, G., Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, N. Y. (1945).

### C. FACTORS CONCERNING DIATOMIC GASES

#### 1. The Divergence Problem

There is an ever-present problem of divergence at high temperatures in the formulas for the thermodynamic functions from statistical mechanics, when one uses them with the usual spectroscopic expression for the energy of a diatomic molecule including anharmonic and vibration-rotation interaction terms. With a potential function such as the Morse function ordinarily used to represent chemical bonding, there results an infinite number of energy states converging to an upper energy limit located at zero potential. The partition function is therefore infinite under all conditions. The energy expression used by spectroscopists consists of only the first few terms of an infinite power series in the rotational

and vibrational quantum numbers, and it should be used only for energies far below the aforementioned convergence limit. Nevertheless, some of these terms, involving the highest powers of the quantum numbers in the expression, are negative and result in positive exponential terms in the partition function, which diverge if carried to large quantum numbers.

In practice, however, one can obtain sufficiently good values for the partition function and derived thermodynamic functions at low temperatures by cutting the series off after a few terms. This approximation becomes progressively worse as the temperature is raised and the divergence increases.

The degree of divergence depends upon the depth of the potential well; and in cases of low binding energy, divergence can be serious at temperatures far below the upper limit of the calculations; namely, 6000°K.

It is very difficult to specify the extent of error introduced by this divergence, and arbitrary cutoff procedures have often been adopted for the divergent terms. However, one is never sure that these cutoff procedures result in better values of the functions at any particular temperature. At low temperatures, the anharmonic, and other, correction terms are unimportant, at intermediate temperatures, they contribute significantly and with sufficient accuracy to be fully retained; and at very high temperatures, one must resort to the uncoupled harmonic oscillator approximation or to an entirely different approach involving cluster integrals.

For the present compilation, the anharmonic, etc., corrections have been fully retained to make low- and intermediate-temperature values of the thermodynamic functions as accurate as possible. Therefore, some inaccuracy undoubtedly exists at the highest temperatures due to the divergence problem; however, it is felt that the values are no worse than those which may have been obtained by neglect of the correction terms or arbitrary cutoff procedures. A concentrated effort has been made to recognize unusual cases where the divergence problem is prohibitively severe below 6000°K.

## 2. Contributions of Higher Electronic States to Thermodynamic Functions of Gaseous Molecules

The lack of a uniform practice relative to the handling of contributions of higher electronic states to the thermodynamic functions of gaseous molecules has generated a minor problem in table consistency in general. This is a problem within sets of tables as well as between sets of tables. However, it is of little consequence to tables based on estimated or inaccurate data because of their low accuracy otherwise.

In the case of gaseous monoxides, the practice in the present work was to use all experimental data available although in some cases, there must be other



electronic levels which add something to the functions at elevated temperatures. When no experimental data were available, spectroscopic constants were estimated for a ground state only. Also, in the case of gaseous dioxide and trioxide calculations, only ground state estimates were made, or reasonably could be made.

Uncertainties of unknown amount can obviously arise if one uses thermodynamic functions of gaseous molecules which contain only ground-state contributions with others which contain contributions of excited electronic states.

In the present work, the practice was adopted of making each table as complete as the data permitted, and an attempt was made to estimate the uncertainties due to incompleteness of data, so that users of the tables will be aware of their limitations. This has the advantage of not hiding uncertainties in a system of consistency, wherein it is hoped that errors will cancel each other. There is no guarantee that the latter will happen. In fact, one could argue that an arbitrary system of consistency may introduce as many errors as it eliminates. The practice used in the present work also has the advantage that tables based on accurate data need not be revised later and that those based on inaccurate or estimated data can be revised when better data become available without disrupting the system.

How can one judge the uncertainties introduced by ignoring excited electronic states? Assume that an equilibrium constant for a vaporization reaction like (IIC2-1) has been measured as a function of temperature over some elevated range of temperature.



The procedure used in the present work was to determine from the measured equilibrium constant an average value of  $\Delta H_{f298}^\circ$  from values calculated at each experimental temperature as in equations (IIC2-2) and (IIC2-3),

$$\Delta H_{f298}^\circ = T\Delta(f.e.f.) + \Delta F_T^\circ \quad , \quad (\text{IIC2-2})$$

$$\Delta H_{f298}^\circ = T\Delta(f.e.f.) - RT \ln K_p \quad , \quad (\text{IIC2-3})$$

in which  $\Delta(f.e.f.)$  is given by equation (III1-4), and the free-energy function of  $\text{MO(g)}$  was calculated without consideration for excited electronic states.

What one is really doing in this case is to find a  $\Delta H_{f298}^\circ$  which forces  $\Delta F_T^\circ$  to come out right over the range of temperature measurement when used with the free-energy functions previously calculated. Usually, the experimental temperature range is sufficiently limited that the temperature dependence of the equilibrium constant will be matched within the uncertainty of the experimental data. However, the calculated  $\Delta F_T^\circ$  will become increasingly bad above or below the experimental temperature range if  $\Delta S_T^\circ$  (actual) is not equal to  $\Delta S_T^\circ$  (calculated) since

$$\left( \frac{\partial \Delta F_T^\circ}{\partial T} \right)_P = - \Delta S_T^\circ \quad . \quad (\text{IIC 2-4})$$

One knows  $\Delta S_T^\circ$  (calculated) from the compilation, and a  $\Delta S_T^\circ$  (actual) over the experimental range of temperature can be found from a Second-Law treatment of the experimental data, consisting of plotting the equilibrium constant versus  $(1/T)$  because of equation (IIC 2-5),

$$- R \ln K_P = \frac{\Delta H_T^\circ}{T} - \Delta S_T^\circ \quad . \quad (\text{IIC 2-5})$$

A comparison of the actual and calculated  $\Delta S_T^\circ$  can help to give an idea of the effect of ignoring excited electronic states in calculating the free-energy function of  $\text{MO(g)}$ , in the range of experimental temperatures at least.

For the JANAF tables<sup>1</sup>, the practice was adopted of neglecting electronic states above  $5000 \text{ cm}^{-1}$ , except in the case of some of the better ("white") tables, such as those for  $\text{O}_2$ .

Brewer has adopted a different practice. He has used "internally consistent" procedures for estimating electronic contributions in both gaseous monoxides<sup>2</sup> and dioxides<sup>3</sup>. This procedure appears to have the advantage of providing a correction of right sign but equally as arbitrary as the others. In some cases, spectroscopic data for the gaseous charged ions required are not available, and approximations must be made to the approximations.

## REFERENCES FOR SECTION IIIC2

1. Dergazarian, T. E. et al, JANAF Interim Thermochemical Tables, Vols. 1 and 2, Dow Chem. Co., Midland, Mich. (31 December 1960).
2. Brewer, L. and M.S. Chandrasekharaiah, Free Energy Functions for Gaseous Monoxides, U.S. At. Energy Comm. Rept. UCRL-8713 (April 1959).
3. Brewer, L., Dissociation energies of gaseous metal dioxides, Chem. Revs. 61, 257 (1961).

### 3. Probable Accuracy of Thermodynamic Functions for Diatomic Gases

During the course of this project, thermodynamic functions for many diatomic gases must be evaluated. Many of the diatomic gases are well characterized regarding their spectral properties, but, on the other hand, many diatomic species; e. g., the transition metal monoxides, still are only incompletely characterized. Since the spectral properties form the basis for the statistical-mechanical method of calculation of thermodynamic properties, it is well to try to develop a guide for estimating the relative importance of these various spectral input data.

In the present report, a later section (IVB30. 4. 1) is devoted to the gaseous molecule  $\text{TiO}$ . For the present purposes, this molecule is used as a reference case and the effects of neglecting or perturbing various input data are noted on the resultant thermodynamic functions. To make the calculations consistent, the same computer program described in the report by Barriault et al<sup>1</sup> is used. The present calculations have used one particular set of input data (HS-60; p. 1-67) for the  $\text{TiO}$  molecule as a reference state. Other sets of input data have been referred to this so-called reference state (HS-60) to note what the resultant perturbations are. It should be noted that the choice of one set of conditions (HS-60) as a reference state is very arbitrary. In fact, this choice differs from the final accepted data used in the thermodynamic table adopted for  $\text{TiO}$  later in this report.

In table 4, an abbreviated summary of the various sets of input data used is presented. A more detailed description of the input data is given in table 5.

TABLE 4

ABBREVIATED SUMMARY OF VARIOUS INPUT DATA USED  
FOR TITANIUM MONOXIDE SPECIES

Case	General Description
HS-56	$X^3\pi; a^1\Delta(581 \text{ cm}^{-1})$
HS-57	$X^3\pi; a^1\Delta(274 \text{ cm}^{-1})$
HS-58	$X^3\pi; a^1\Delta(804 \text{ cm}^{-1})$
HS-59	$X^3\pi; a^1\Delta(581 \text{ cm}^{-1}); ^1\pi(11853 \text{ cm}^{-1})$
HS-60	$X^3\pi$
HS-61	$X^3\pi$ ; Same as HS-60 except decrease $\omega_e$ by $100 \text{ cm}^{-1}$
HS-62	$X^3\pi$ ; Same as HS-60 except make $x_e \omega_e = 0.0$
HS-63	$X^3\pi$ ; Same as HS-60 except make $\alpha_e = 0.0$
HS-64	$X^3\pi$ ; Same as HS-60 except make $B_e$ smaller by 10 percent
HS-65	$X^3\pi$ ; Same as HS-60 except make $D_e = 0.0$
HS-66	Radical perturbation; Assume ground state has $g = 2$
HS-67	$X^3\pi; a^1\Delta(581 \text{ cm}^{-1}); ^1\Sigma(1708 \text{ cm}^{-1}); b^1\pi(10814 \text{ cm}^{-1})$
HS-68	Brewer and Chandrasekharaiah <sup>2</sup> approximation using two lowest atomic states of $\text{Ti}^{+2}$

TABLE 5DETAILED SUMMARY OF INPUT DATA USED FOR  
TITANIUM MONOXIDE SPECIES

## HS-56

$E \text{ (cm}^{-1}\text{)}$	0.0	66.7	141.3	581.0
$g$	2.0	2.0	2.0	2.0
$\omega_e \text{ (cm}^{-1}\text{)}$	1008.6	1008.6	1008.6	1009.6
$\omega_e x_e \text{ (cm}^{-1}\text{)}$	4.61	4.61	4.61	0.0
$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0
$B_e \text{ (cm}^{-1}\text{)}$	0.5355	0.5355	0.5355	0.5362
$\alpha_e \text{ (cm}^{-1}\text{)}$	0.0031	0.0031	0.0031	0.0
$\gamma_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0
$D_e \text{ (cm}^{-1}\text{)}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.04 \times 10^{-7}$

## HS-57

Same as HS-56 except in fourth column, for E, 581.0 is replaced by 274.0  $\text{cm}^{-1}$

## HS-58

Same as HS-56 except in fourth column, for E, 581.0 is replaced by 804.0  $\text{cm}^{-1}$

TABLE 5 (Cont'd)

## HS-59

First four columns are same as HS-56; then add a fifth column as follows	
$E \text{ (cm}^{-1}\text{)}$ 11853.0	$\omega_e y_e \text{ (cm}^{-1}\text{)}$ 0.0
$g$ 2.0	$B_e \text{ (cm}^{-1}\text{)}$ 0.512
$\omega_e \text{ (cm}^{-1}\text{)}$ 1000.0	$\alpha_e \text{ (cm}^{-1}\text{)}$ 0.0
$\omega_e x_e \text{ (cm}^{-1}\text{)}$ 0.0	$\gamma_e \text{ (cm}^{-1}\text{)}$ 0.0
	$D_e \text{ (cm}^{-1}\text{)}$ 0.0

## HS-60

 $X^3\Pi$  GROUND STATE ONLY

$E \text{ (cm}^{-1}\text{)}$	0.0	66.7	141.3
$g$	2.0	2.0	2.0
$\omega_e \text{ (cm}^{-1}\text{)}$	1008.6	1008.6	1008.6
$\omega_e x_e \text{ (cm}^{-1}\text{)}$	4.61	4.61	4.61
$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0
$B_e \text{ (cm}^{-1}\text{)}$	0.5355	0.5355	0.5355
$\alpha_e \text{ (cm}^{-1}\text{)}$	0.0031	0.0031	0.0031
$\gamma_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0
$D_e \text{ (cm}^{-1}\text{)}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$

## HS-61

Same as HS-60 except perturb  $\omega_e$  by replacing 1008.6 by 908.6  $\text{cm}^{-1}$  in all three columns

TABLE 5 (Cont'd)

HS-62

Same as HS-60 except perturb  $\omega_e x_e$  by replacing 4.61 by 0.0  $\text{cm}^{-1}$  in all three columns

HS-63

Same as HS-60 except perturb  $\alpha_e$  by replacing 0.0031 by 0.0  $\text{cm}^{-1}$  in all three columns

HS-64

Same as HS-60 except make  $B_e$  smaller by 10 percent; i. e., by replacing 0.5355 by 0.482  $\text{cm}^{-1}$  in all three columns

HS-65

Same as HS-60 except replace  $D_e$  values of  $6.03 \times 10^{-7}$  by 0.0  $\text{cm}^{-1}$  in all three columns

HS-66

For this state, a completely new assumption is made regarding the electronic ground state

$E$ ( $\text{cm}^{-1}$ )	0.0
$g$	2.0
$\omega_e$ ( $\text{cm}^{-1}$ )	1008.6
$\omega_e x_e$ ( $\text{cm}^{-1}$ )	4.61
$\omega_e y_e$ ( $\text{cm}^{-1}$ )	0.0
$B_e$ ( $\text{cm}^{-1}$ )	0.5355
$\alpha_e$ ( $\text{cm}^{-1}$ )	0.0031
$\gamma_e$ ( $\text{cm}^{-1}$ )	0.0
$D_e$ ( $\text{cm}^{-1}$ )	$6.03 \times 10^{-7}$

TABLE 5 (Concl'd)

HS-67

$E \text{ (cm}^{-1}\text{)}$	0.0	66.7	141.3	581.0	1708.0	10814.0
$g$	2.0	2.0	2.0	2.0	1.0	2.0
$\omega_e \text{ (cm}^{-1}\text{)}$	1008.6	1008.6	1008.6	1009.6	1023.8	918.7
$\omega_e x_e \text{ (cm}^{-1}\text{)}$	4.61	4.61	4.61	0.0	4.64	3.75
$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0	0.0	0.0
$B_e \text{ (cm}^{-1}\text{)}$	0.5355	0.5355	0.5355	0.5362	0.5490	0.513
$\alpha_e \text{ (cm}^{-1}\text{)}$	0.0031	0.0031	0.0031	0.0	0.00337	0.0029
$\gamma_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0	0.0	0.0
$D_e \text{ (cm}^{-1}\text{)}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.04 \times 10^{-7}$	0.0	0.0

HS-68

(Use Brewer and Chandrasekharan<sup>2</sup> Approximation)

$E \text{ (cm}^{-1}\text{)}$	0.0	183.7	421.9	8472.6
$g$	5.0	7.0	9.0	5.0
$\omega_e \text{ (cm}^{-1}\text{)}$	1008.1	1008.1	1008.1	1008.1
$\omega_e x_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0
$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0
$B_e \text{ (cm}^{-1}\text{)}$	0.5355	0.5355	0.5355	0.5355
$\alpha_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0
$\gamma_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0
$D_e \text{ (cm}^{-1}\text{)}$	0.0	0.0	0.0	0.0



### a. Effects of Choice of Electronic States

It is well known that the presence of unknown low-lying electronic states can lead to appreciable uncertainties in the thermodynamic functions. Thus, Brewer and Chandrasekharaiah<sup>2</sup> have noted that even the ground state may not be known for many transition metal oxides. To illustrate the effects of considering various possible electronic states, cases HS-56, HS-57, HS-58, HS-59, HS-60, HS-66, HS-67 and HS-68 are appropriate. The first three cases, HS-56 to HS-58, illustrate the effect of the fact that the  $a^1\Delta$  state has been determined to a low degree of accuracy. Thus, Phillips<sup>3</sup> has indicated that the  $a^1\Delta$  state may be 274 to 804  $\text{cm}^{-1}$  above the ground state. The average level is, thus, 581  $\text{cm}^{-1}$  above the ground level. It is to be noted that the same set of vibrational and rotational constants are used for cases HS-56 to HS-58. For the ground state ( $^3\pi$ ),  $\omega_e$  has been taken from Herzberg<sup>4</sup> although the value of 1008.4  $\text{cm}^{-1}$  has been corrected to 1008.6  $\text{cm}^{-1}$  to account for the natural isotopic mixture. It will later be seen that such a change produces very small effects on the thermodynamic functions.

Other spectral constants from Herzberg<sup>4</sup> include  $\omega_e$ ,  $x_e$ ,  $B_e$ , and  $\alpha_e$ .  $D_e$  has been estimated from the relation  $D_e = \frac{4 B_e^3}{\omega_e^2}$ .

For the  $a^1\Delta$  state, the values of  $\omega_e$ ,  $B_e$ , and  $D_e$  have been estimated. The value of  $r_e = 1.619 \text{ \AA}$  has been taken from Herzberg and used to calculate  $\omega_e$ , using the relation  $r_e \omega_e^2 = \text{constant}$  for all electronic states.  $B_e$  has been calculated from the internuclear distance, and  $D_e$  has been estimated

$$\text{by } D_e = \frac{4 B_e^3}{\omega_e^2}.$$

For HS-59, the data of HS-56 have been repeated, but, in addition, the effect of a  $^1\pi$  excited electronic state is also considered. From Rosen,<sup>5</sup> this state is listed as 11272  $\text{cm}^{-1}$  above the  $^1\Delta$  state, and, thus, the energy level referred to the zero vibration state of the ground state becomes  $11272 + 581.0 = 11853 \text{ cm}^{-1}$  if one neglects the small effect due to zero-point vibrational energy. The value of  $\omega_e$  has been estimated, and  $B_e$  has been taken from Rosen.<sup>5</sup>

For HS-60, the effect of a single electronic ground state  $X^3\pi$  as listed by Rosen<sup>5</sup> and Herzberg<sup>4</sup> is considered. Other spectroscopic constants are kept the same as for the previous cases (HS-56 to HS-58).

For HS-66, the effect of an entirely different ground state is considered. That is, the effect of discovering a new ground state of degeneracy 2 with no other low-lying levels is considered. Spectroscopic constants,

such as  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ ,  $\alpha_e$ , and  $D_e$ , are kept the same as for HS-56. It is to be noted that this case is purely hypothetical. This hypothetical case comes closer to resembling a suggestion by Berg and Sinanoglu<sup>6</sup> that the expected ground state for  $\text{TiO(g)}$  is  $^3\Sigma$  rather than the commonly accepted  $^3\Pi$ . The Berg and Sinanoglu case would correspond to degeneracy 3 rather than 2 as used in the present calculations however.

For HS-67, the effect of considering additional low-lying states found by Pettersson and Lindgren<sup>7</sup> is considered. They have reported a  $d^1\Sigma$  state at  $1708 \text{ cm}^{-1}$  and a  $b^1\Pi$  state at  $10814.4 \text{ cm}^{-1}$ . Their reported values for  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ , and  $\alpha_e$  are utilized.

For HS-68, the effect of using the simple ionic model suggested by Brewer and Chandrasekharaiah<sup>2</sup> is tested. In this case, the electronic energy levels for the  $\text{TiO}$  molecule are estimated by using the electronic levels for the  $\text{Ti}^{+2}$  ion as given by Moore.<sup>8</sup> The states which Moore lists for  $\text{Ti III}$  are shown below:

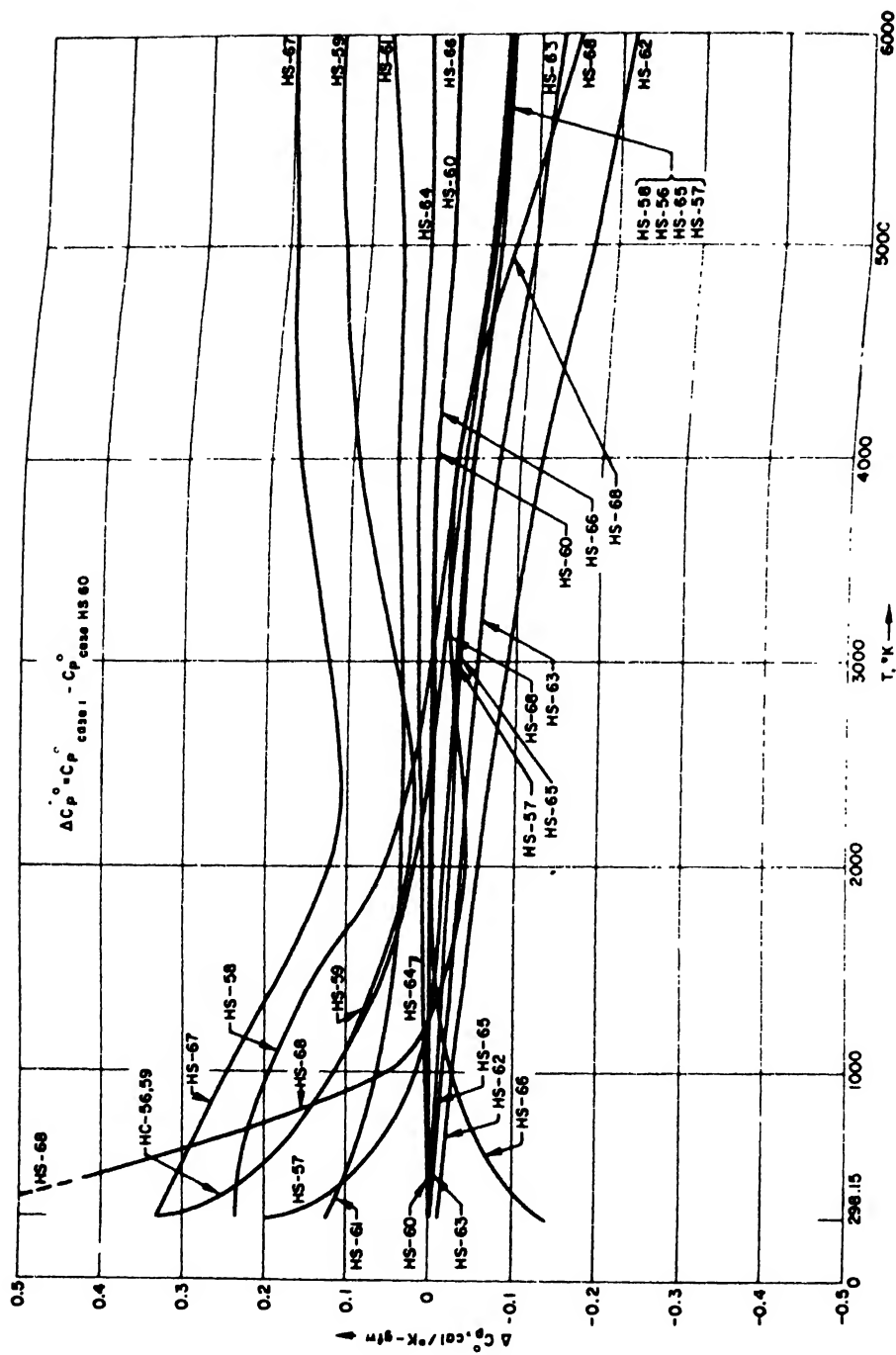
Designation	J	Level $\text{cm}^{-1}$
$a^3F$	2	0.0
	3	183.7
	4	421.9
$a^1D$	2	8472.6

To compare the different data obtained by different choices of electronic states and subsequent cases as well, refer to table 6. Here, the absolute values of  $C_p^\circ$ ,  $S^\circ$ ,  $-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)$ , and  $H_T^\circ - H_{298.15}^\circ$  are

tabulated at temperatures of  $298.15^\circ$ ,  $1000^\circ$ ,  $2000^\circ$ ,  $3000^\circ$ ,  $4000^\circ$ ,  $5000^\circ$ , and  $6000^\circ\text{K}$ . In table 7, the differences between the data for a given case and that for HS-60 used as a reference are shown. The data from table 7 have also been plotted in figures 21 to 24.

From the plotted data in figure 21, it is seen that the data for  $C_p^\circ$  are fairly well localized with maximum variations of about  $\pm 0.3 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

In the case of entropy and free-energy functions, it is seen that appreciable variations can occur. Entropy data for HS-67 (the data actually preferred for  $\text{TiO}$  in the thermodynamic tables) are  $0.572 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  larger than for HS-60 at  $1000^\circ\text{K}$ , whereas that for HS-68 (the Brewer and Chandrasekharaiah<sup>2</sup> approximation) is  $2.384 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  larger than that for HS-60. These types of results are to be expected since more



**Figure 21** HEAT-CAPACITY DIFFERENCES VERSUS TEMPERATURE  
FOR  $\text{TiO}_2(\text{g})$

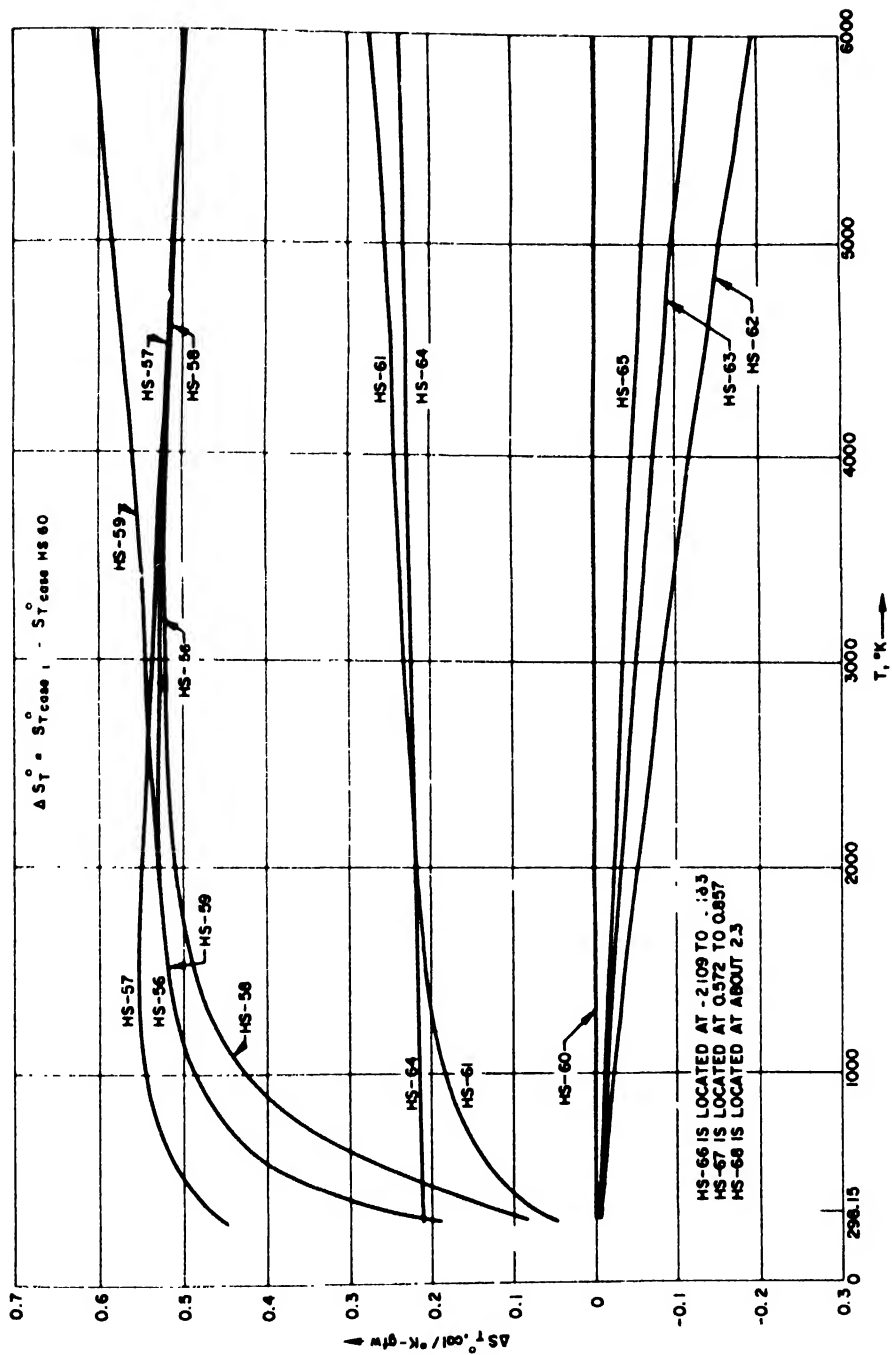


Figure 22 ENTROPY DIFFERENCES VERSUS TEMPERATURE FOR  $\text{TiO(g)}$

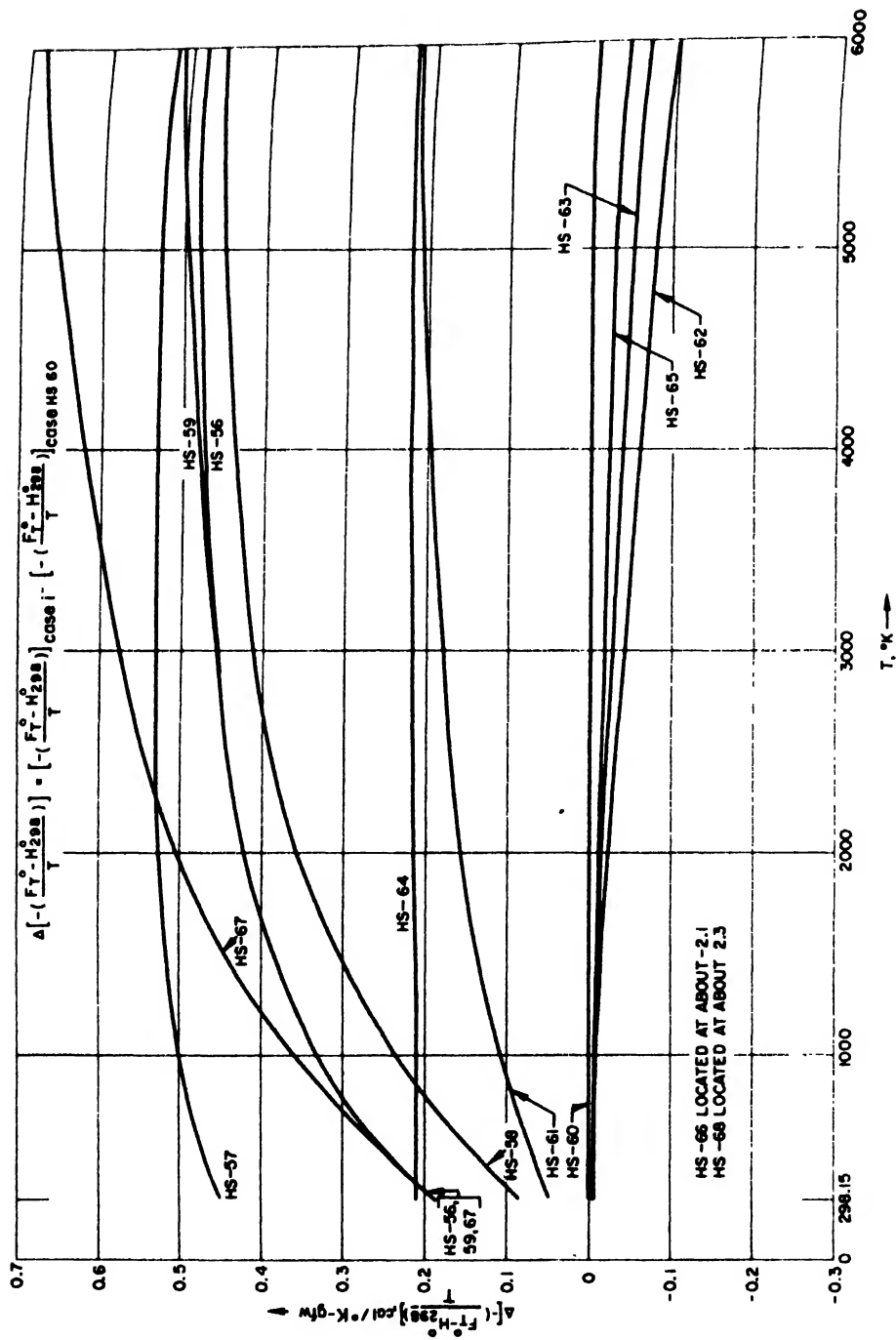


Figure 23 FREE-ENERGY FUNCTION DIFFERENCES VERSUS TEMPERATURE FOR  $\text{TiO(g)}$

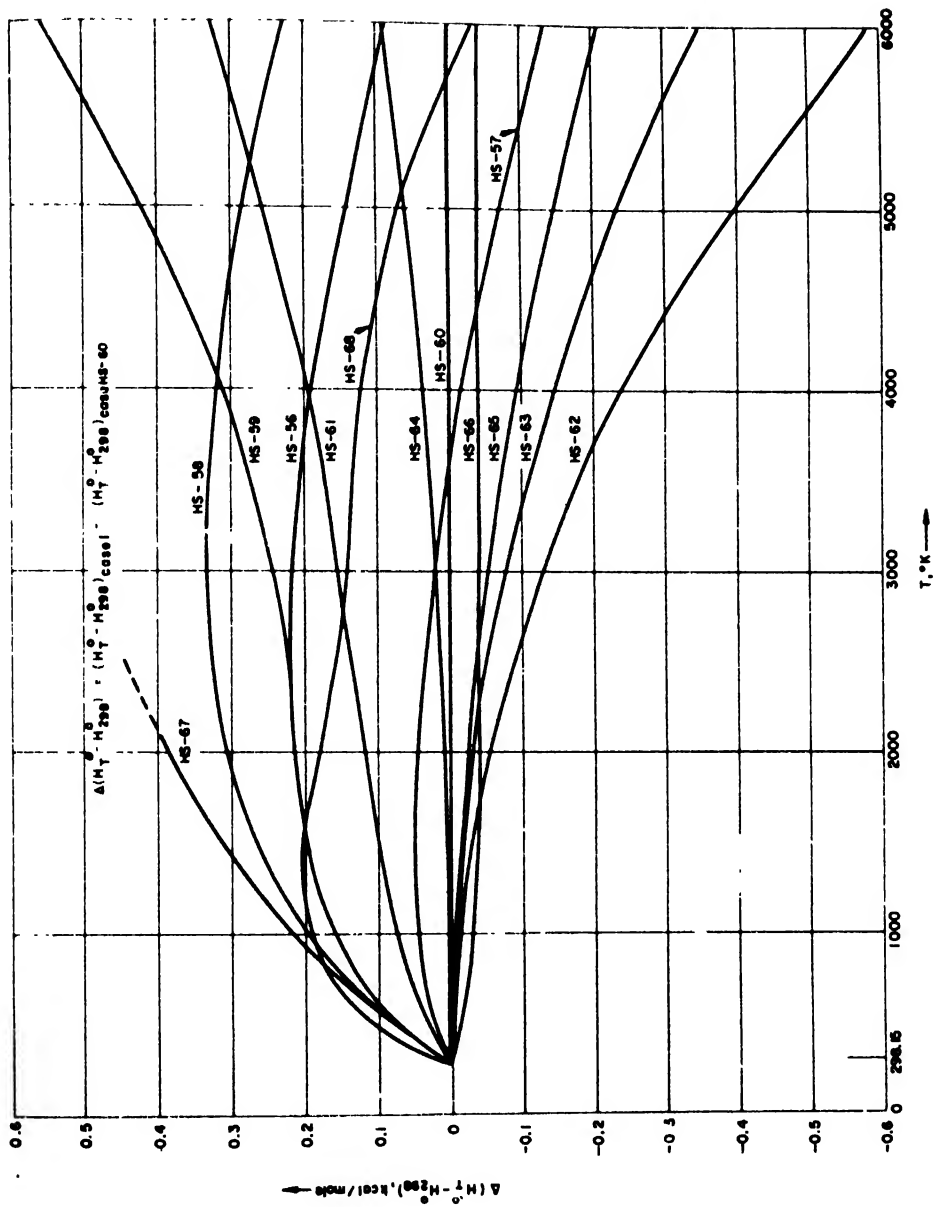


Figure 24 ENTHALPY-CONTENT DIFFERENCES VERSUS TEMPERATURE  
FOR  $\text{TiO}_{(g)}$

relatively low-lying electronic levels are being considered in the cases of HS-67 and HS-68. The effect of additional states is naturally to increase the entropy. In figure 22, the changes in entropy versus temperature for various cases are shown.

Effects on the free-energy functions are produced which are also similar to those already noted for the entropy. Figure 23 illustrates the data obtained.

In the case of enthalpy contents, it is found that the data vary by about  $\pm 0.5$  kcal/mole over the range of 298.15° to 6000°K. The variation is shown in figure 24.

#### b. Effect of Choice of Vibrational and Rotational Constants

In a given electronic level, it is found that the energy levels for a vibrating rotator are spaced according to the following scheme (see e. g., Herzberg, <sup>4</sup> p. 107):

$$\begin{aligned} \nu = & \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \dots \\ & + B_v J (J + 1) - D_v J^2 (J + 1)^2 + \dots, \end{aligned}$$

here  $\nu$  = energy ( $\text{cm}^{-1}$ ),

$\omega_e$  = vibrational frequency,

$v$  = vibrational quantum number,

$\omega_e x_e$  = anharmonicity constant ( $\text{cm}^{-1}$ ),

$\omega_e y_e$  = higher-order anharmonicity constant,

$B_v$  = rotational constant in vibrational state  $v$ ; i. e.,

$B_v = B_e - \alpha_e (v + 1/2) + \gamma_e (v + 1/2)^2 + \dots$ ,

where  $B_e$  = rotational constant for the equilibrium separation of atoms,

$\alpha_e$  = vibrational-rotational coupling constant,

$\gamma_e$  = higher-order term to correct rotational constant  $B_e$ ,

$D_v$  = mean rotational constant (also called stretching constant) representing the effect of centrifugal force,

$D_v = D_e + \beta_e (v + 1/2) + \dots$ , and

$\beta_e$  = higher-order correction term to  $D_e$  (usually so small that it can be ignored).

To test the effect of changes in these vibrational-rotational constants, several cases have been studied. They include effects of changes on  $\omega_e$  the vibrational frequency (HS-61), on  $\omega_e x_e$  the anharmonicity constant (HS-62), on  $\alpha_e$  the vibrational-rotational coupling constant (HS-63), on  $B_e$  the rotational constant (HS-64), and on  $D_e$  the stretching constant (HS-65).

In figure 22, it is seen that a reduction of  $100 \text{ cm}^{-1}$  in  $\omega_e$  (HS-61) causes an increase in the entropy of about  $0.2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . An effect of about the same magnitude is caused by a 10-percent reduction of  $B_e$  (HS-64).

It can be seen that the constants  $\omega_e x_e$ ,  $\alpha_e$ , and  $D_e$  are much less significant since replacing their values of case HS-60 by 0.0 still only leads to decreases in the entropy of about  $0.1 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . In the case of the  $\omega_e x_e$  perturbation (HS-62), the entropy is decreased by  $-0.194 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  at  $6000^\circ\text{K}$ .

From the data thus presented, it is possible to have a better feeling for the relative importance of the various spectroscopic constants. The data clearly show the importance of the various electronic states. When the knowledge of such electronic states is inadequate, there is usually not much reason for evaluating the second-order spectroscopic constants.

TABLE 6

THERMODYNAMIC DATA FOR TITANIUM MONOXIDE (gas)  
FOR VARIOUS INPUT CASES  
(All Quantities in  $\text{cal deg K}^{-1} \text{ gfw}^{-1}$ )

Temperature $^\circ\text{K}$	Case	$C_p^\circ$	$S_T^\circ$	$\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$
298.15	HS-56	7.808	55.988	55.988	0.000
298.15	HS-57	7.678	56.250	56.250	0.000
298.15	HS-58	7.716	55.886	55.886	0.000
298.15	HS-59	7.808	55.988	55.988	0.000
298.15	HS-60	7.482	55.802	55.802	0.000
298.15	HS-61	7.607	55.849	55.849	0.000
298.15	HS-62	7.472	55.799	55.799	0.000
298.15	HS-63	7.480	55.796	55.796	0.000
298.15	HS-64	7.483	56.013	56.013	0.000
298.15	HS-65	7.479	55.799	55.799	0.000
298.15	HS-66	7.339	53.693	53.693	0.000
298.15	HS-67	7.814	55.989	55.989	0.000
298.15	HS-68	8.296	57.767	57.767	0.000



TABLE 6 (Cont'd)

Temperature °K	Case	$C_p^\circ$	$S_T^\circ$	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$
1000	HS-56	8.814	66.137	60.180	5.957
1000	HS-57	8.712	66.197	60.352	5.845
1000	HS-58	8.893	66.078	60.085	5.993
1000	HS-59	8.814	66.137	60.180	5.957
1000	HS-60	8.697	65.649	59.850	5.799
1000	HS-61	8.760	65.835	59.961	5.873
1000	HS-62	8.669	65.623	59.839	5.785
1000	HS-63	8.680	65.633	59.841	5.792
1000	HS-64	8.701	65.863	60.062	5.801
1000	HS-65	8.685	65.637	59.844	5.793
1000	HS-66	8.683	63.473	57.705	5.768
1000	HS-67	8.941	66.221	60.206	6.014
1000	HS-68	8.748	68.033	62.042	5.990
2000	HS-56	8.994	72.317	64.876	14.882
2000	HS-57	8.960	72.333	64.977	14.711
2000	HS-58	9.029	72.297	64.811	14.973
2000	HS-59	9.002	72.318	64.876	14.884
2000	HS-60	8.975	71.786	64.452	14.668
2000	HS-61	9.009	72.003	64.610	14.785

TABLE 6 (Cont'd)

Temperature °K	Case	C <sub>p</sub> <sup>°</sup>	S <sub>T</sub> <sup>°</sup>	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	H <sub>T</sub> <sup>°</sup> - H <sub>298</sub> <sup>°</sup>
2000	HS-62	8.917	71.732	64.426	14.612
2000	HS-63	8.940	71.752	64.435	14.635
2000	HS-64	8.984	72.005	64.666	14.677
2000	HS-65	8.952	71.763	64.440	14.645
2000	HS-66	8.971	69.605	62.290	14.630
2000	HS-67	9.097	72.482	64.954	15.055
2000	HS-68	8.932	74.163	66.741	14.844
3000	HS-56	9.068	75.979	68.007	23.915
3000	HS-57	9.052	75.985	68.079	23.721
3000	HS-58	9.087	75.970	67.959	24.032
3000	HS-59	9.126	75.991	68.009	23.946
3000	HS-60	9.083	75.448	67.548	23.701
3000	HS-61	9.121	75.679	67.728	23.854
3000	HS-62	8.991	75.364	67.507	23.570
3000	HS-63	9.027	75.395	67.521	23.623
3000	HS-64	9.097	75.671	67.764	23.722
3000	HS-65	9.048	75.413	67.530	23.649
3000	HS-66	9.081	73.265	65.378	23.661
3000	HS-67	9.205	76.190	68.122	24.203
3000	HS-68	9.059	77.809	69.862	23.842

TABLE 6 (Cont'd)

Temperature °K	Case	$C_p^\circ$	$S_T^\circ$	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$
4000	HS-56	9.131	78.597	70.344	33.015
4000	HS-57	9.121	78.600	70.398	32.808
4000	HS-58	9.142	78.593	70.306	33.146
4000	HS-59	9.259	78.636	70.351	33.139
4000	HS-60	9.166	78.074	69.868	32.826
4000	HS-61	9.216	78.319	70.063	33.022
4000	HS-62	9.036	77.957	69.810	32.585
4000	HS-63	9.088	78.001	69.831	32.681
4000	HS-64	9.186	78.303	70.086	32.865
4000	HS-65	9.120	78.027	69.844	32.733
4000	HS-66	9.165	75.891	67.695	32.785
4000	HS-67	9.330	78.857	70.489	33.471
4000	HS-68	9.138	80.428	72.191	32.945
5000	HS-56	9.193	80.644	72.209	42.176
5000	HS-57	9.186	80.645	72.253	41.962
5000	HS-58	9.200	80.641	72.178	42.316
5000	HS-59	9.374	80.717	72.226	42.457
5000	HS-60	9.245	80.131	71.725	42.032
5000	HS-61	9.309	80.390	71.933	42.285

TABLE 6 (Concl'd)

Temperature °K	Case	$C_p^\circ$	$S_T^\circ$	$\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$
5000	HS-62	9.074	79.977	71.649	41.641
5000	HS-63	9.143	80.035	71.675	41.797
5000	HS-64	9.271	80.365	71.946	42.094
5000	HS-65	9.187	80.073	71.695	41.887
5000	HS-66	9.245	77.948	69.550	41.990
5000	HS-67	9.439	80.953	72.382	42.857
5000	HS-68	9.171	82.471	74.050	42.103
6000	HS-56	9.257	82.329	73.763	51.401
6000	HS-57	9.252	82.330	73.799	51.181
6000	HS-58	9.262	82.328	73.737	51.547
6000	HS-59	9.466	82.438	73.792	51.878
6000	HS-60	9.326	81.829	73.276	51.317
6000	HS-61	9.407	82.104	73.497	51.642
6000	HS-62	9.109	81.635	73.179	50.732
6000	HS-63	9.197	81.707	73.212	50.967
6000	HS-64	9.357	82.068	73.500	51.408
6000	HS-65	9.256	81.759	73.241	51.108
6000	HS-66	9.325	79.646	71.100	51.275
6000	HS-67	9.526	82.686	73.963	52.341
6000	HS-68	9.176	84.144	75.597	51.279

TABLE 7

THERMODYNAMIC FUNCTION DIFFERENCES  $(\Delta C_p^\circ, \Delta S_T^\circ, \Delta \left[ -\left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right])$ ,

$\Delta(H_T^\circ - H_{298.15}^\circ)$  FOR TITANIUM MONOXIDE (gas) AT  
VARIOUS TEMPERATURES  
[HS60 as Basic State; e.g.,  $\Delta C_p^\circ = C_p^\circ(\text{case i}) - C_p^\circ(\text{case HS60})$ ]  
(All Quantities in cal deg K<sup>-1</sup> gfw<sup>-1</sup>)

Temperature °K	Case	$\Delta C_p^\circ$	$\Delta S_T^\circ$	$\Delta - \left[ \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right]$	$\Delta(H_T^\circ - H_{298}^\circ)$
298.15	HS-56	0.326	0.186	0.186	0.0
298.15	HS-57	0.196	0.448	0.448	0.0
298.15	HS-58	0.234	0.084	0.084	0.0
298.15	HS-59	0.326	0.186	0.186	0.0
298.15	HS-60	0.0	0.0	0.0	0.0
298.15	HS-61	0.125	0.047	0.047	0.0
298.15	HS-62	-0.010	-0.003	-0.003	0.0
298.15	HS-63	-0.002	-0.006	-0.006	0.0
298.15	HS-64	0.001	0.211	0.211	0.0
298.15	HS-65	-0.003	-0.003	-0.003	0.0
298.15	HS-66	-0.143	-2.109	-2.109	0.0
298.15	HS-67	0.332	0.187	0.187	0.0
298.15	HS-68	0.814	1.965	1.965	0.0
1000	HS-56	0.117	0.488	0.330	0.158
1000	HS-57	0.015	0.548	0.502	0.046
1000	HS-58	0.196	0.429	0.235	0.194
1000	HS-59	0.117	0.488	0.330	0.158

TABLE 7 (Cont'd)

Temperature °K	Case	$\Delta C_p^\circ$	$\Delta S_T^\circ$	$\Delta \left[ \frac{(F_T^\circ - H_{298}^\circ)}{T} \right]$	$\Delta (H_T^\circ - H_{298}^\circ)$
1000	HS-60	0.0	0.0	0.0	0.0
1000	HS-61	0.063	0.186	0.111	0.074
1000	HS-62	-0.028	-0.026	-0.011	-0.014
1000	HS-63	-0.017	-0.016	-0.009	-0.007
1000	HS-64	0.004	0.214	0.212	0.002
1000	HS-65	-0.012	-0.012	-0.006	-0.006
1000	HS-66	-0.014	-2.176	-2.145	-0.031
1000	HS-67	0.244	0.572	0.356	0.215
1000	HS-68	0.051	2.384	2.192	0.191
2000	HS-56	0.019	0.531	0.424	0.214
2000	HS-57	-0.015	0.547	0.525	0.043
2000	HS-58	0.054	0.511	0.359	0.305
2000	HS-59	0.027	0.532	0.424	0.216
2000	HS-60	0.0	0.0	0.0	0.0
2000	HS-61	0.034	0.217	0.158	0.117
2000	HS-62	-0.058	-0.054	-0.026	-0.056
2000	HS-63	-0.035	-0.034	-0.017	-0.033
2000	HS-64	0.009	0.219	0.214	0.009
2000	HS-65	-0.023	-0.023	-0.012	-0.023
2000	HS-66	-0.004	-2.181	-2.162	-0.038
2000	HS-67	0.122	0.696	0.502	0.387
2000	HS-68	-0.043	2.377	2.289	0.176

TABLE 7 (Cont'd)

Temperature °K	Case	$\Delta C_p^\circ$	$\Delta S_T^\circ$	$\Delta \left[ \frac{F_T^\circ - H_{298}^\circ}{T} \right]$	$\Delta (H_T^\circ - H_{298}^\circ)$
3000	HS-56	-0.015	0.531	0.459	0.214
3000	HS-57	-0.031	0.537	0.531	0.020
3000	HS-58	0.004	0.522	0.411	0.331
3000	HS-59	0.043	0.543	0.461	0.245
3000	HS-60	0.0	0.0	0.0	0.0
3000	HS-61	0.038	0.231	0.180	0.153
3000	HS-62	-0.092	-0.084	-0.041	-0.131
3000	HS-63	-0.056	-0.053	-0.027	-0.078
3000	HS-64	0.014	0.223	0.216	0.021
3000	HS-65	-0.035	-0.035	-0.018	-0.052
3000	HS-66	-0.002	-2.183	-2.170	-0.040
3000	HS-67	0.122	0.742	0.574	0.502
3000	HS-68	-0.024	2.361	2.314	0.141
4000	HS-56	-0.035	0.523	0.476	0.189
4000	HS-57	-0.045	0.526	0.530	-0.018
4000	HS-58	-0.024	0.519	0.438	0.320
4000	HS-59	0.093	0.562	0.483	0.313
4000	HS-60	0.0	0.0	0.0	0.0
4000	HS-61	0.050	0.245	0.195	0.196
4000	HS-62	-0.130	-0.117	-0.058	-0.241
4000	HS-63	-0.078	-0.073	-0.037	-0.145

TABLE 7 (Cont'd)

Temperature °K	Case	$\Delta C_p^\circ$	$\Delta S_T^\circ$	$\Delta \left[ \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right]$	$\Delta (H_T^\circ - H_{298}^\circ)$
4000	HS-64	0.020	0.229	0.218	0.039
4000	HS-65	-0.046	-0.047	-0.024	-0.093
4000	HS-66	-0.001	-2.183	-2.173	-0.041
4000	HS-67	0.164	0.783	0.621	0.645
4000	HS-68	-0.028	2.354	2.323	0.119
5000	HS-56	-0.052	0.513	0.484	0.144
5000	HS-57	-0.059	0.514	0.528	-0.070
5000	HS-58	-0.045	0.510	0.453	0.284
5000	HS-59	0.129	0.586	0.501	0.425
5000	HS-60	0.0	0.0	0.0	0.0
5000	HS-61	0.064	0.259	0.208	0.253
5000	HS-62	-0.171	-0.154	-0.076	-0.391
5000	HS-63	-0.102	-0.096	-0.050	-0.235
5000	HS-64	0.026	0.234	0.221	0.062
5000	HS-65	-0.058	-0.058	-0.030	-0.145
5000	HS-66	0.0	-2.183	-2.175	-0.042
5000	HS-67	0.194	0.822	0.657	0.825
5000	HS-68	-0.074	2.340	2.325	0.071



TABLE 7 (Concl'd)

Temperature °K	Case	$\Delta C_p^\circ$	$\Delta S_T^\circ$	$\Delta \left[ \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right]$	$\Delta (H_T^\circ - H_{298}^\circ)$
6000	HS-56	-0.069	0.500	0.487	0.084
6000	HS-57	-0.074	0.501	0.523	-0.136
6000	HS-58	-0.064	0.499	0.461	0.230
6000	HS-59	0.140	0.609	0.516	0.561
6000	HS-60	0.0	0.0	0.0	0.0
6000	HS-61	0.081	0.275	0.221	0.325
6000	HS-62	-0.217	-0.194	-0.097	-0.585
6000	HS-63	-0.129	-0.122	-0.064	-0.350
6000	HS-64	0.031	0.239	0.224	0.091
6000	HS-65	-0.070	-0.070	-0.035	-0.209
6000	HS-66	-0.001	-2.183	-2.176	-0.042
6000	HS-67	0.200	0.857	0.687	1.024
6000	HS-68	-0.150	2.315	2.321	-0.038

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#### D. ESTIMATION OF LOW-TEMPERATURE HEAT CAPACITY AND ENTROPY AT 298.15°K FOR BORIDES, CARBIDES, AND NITRIDES

##### 1. General

For many of the refractory compounds of interest in this project, there does not exist the required experimental low-temperature heat-capacity data to yield reliable values of entropy at room temperature; i. e.,  $S_{298.15}^{\circ}$  values are not available. Recent vaporization studies by Leitnaker *et al.*<sup>1</sup> for  $ZrB_2$  and by Schissel and Trulson<sup>2</sup> for  $TiB_2$  were hampered because of lack of accurate free-energy functions for these diboride materials, and they were forced to make an approximation by adding the contributions of the separate elements. The recent experimental low-temperature heat-capacity measurements for  $ZrB_2$  by Westrum<sup>3</sup> indicated that the  $S_{298}^{\circ}$  value for  $ZrB_2$  is substantially lower than is given by the approximation used by Leitnaker *et al.*<sup>1</sup> The effect of the accurate free-energy function is to add about 6 kcal to the heat of vaporization of  $ZrB_2$ . In the case of  $TiB_2$ , there are still no experimental data; however, by various techniques, more realistic estimates of its entropy at 298.15 can be made as discussed in the section on  $TiB_2$ . There the effect of using more accurate free-energy function causes an effective increase of the heat of vaporization of  $TiB_2$  from the 430 kcal calculated by Schissel and Trulson to 441 kcal, i. e., the correction amounts to 11 kcal.

In any estimation procedure, it is advisable to use as many separate, independent determinations as possible. Recently, Mezaki *et al.*<sup>4</sup> have applied the Latimer<sup>5</sup> technique to estimating the entropy for several borides. In this method, it is necessary to have experimental data for at least one boride. Altman and Margrave<sup>6</sup> have also used a technique whereby Debye and Einstein functions are used to join with experimental high-temperature heat-capacity data and thus estimate  $S_{298}^{\circ}$ . Kaufman<sup>7</sup> has also used a scheme for estimating entropies based on the use of Debye functions. His method of summing contributions differs from the method reported below.

For the present work, a method of using Debye functions as described by Krestovnikov and Vendrikh<sup>8</sup> has been applied. The last workers had used their technique to estimate  $S_{298.15}^{\circ}$ ,  $TiB_2$  = 7.52 e. u.

In the present method, the effective heat-capacity contributions at constant volume are calculated separately for each element in the compound. Thus, a Debye theta is calculated for each element separately. The individual Debye contributions are then summed to give the total heat capacity at constant volume. This is then corrected from  $C_V$  to  $C_p^\circ$  by the empirical Nernst relation, and the resulting  $C_p^\circ$  data are integrated from  $0^\circ$  to  $298.15^\circ\text{K}$  to give an  $S_{298.15}^\circ$  value.

To calculate the effective Debye temperature of a given element, the Lindemann relation is used:

$$\theta_i = K \left( \frac{T_i}{M_i} \right)^{1/2} V_i^{-1/3} ,$$

where  $\theta_i$  = Debye  $\theta$  for  $i$  th element in the elemental state,

$K$  = Lindemann constant,

$T_i$  = Melting point of pure element  $i$ ,

$M_i$  = Molecular weight of  $i$  th element, and

$V_i$  = atomic volume,  $\text{cm}^3$  of  $i$  th element.

For the Lindemann constant, Krestovnikov and Vendrikh had used  $K = 135$ . However, for most of the present calculations, a value of  $K = 137$  from Zemansky<sup>9</sup> was used.

To obtain the effective Debye temperature  $\theta_i'$  in the compound state, the relation used becomes

$$\theta_i' = \theta_i \left( \frac{T_c}{T_i} \right)^{1/2} ,$$

where  $\theta_i$  = Debye temperature for pure element  $i$ ,

$T_c$  = melting point of compound, and

$T_i$  = melting point of element  $i$ ,

It can be shown from the above equations that

$$\theta_i' = K \left( \frac{T_c}{M_i} \right)^{1/2} V_i^{-1/3} .$$

Hence, the only input data to calculate the entropy of a compound are its melting point in  $^\circ\text{K}$  and the molecular weights and atomic volumes for the individual pure elements. Melting-point data for the pure elements are necessary only to calculate  $\theta_i$  quantities, but are not essential for the calculation of the  $\theta_i'$  quantities.

To convert constant-volume heat capacity to constant-pressure heat capacity, the Nernst-Lindemann<sup>10</sup> relation is used:

$$C_p^\circ = C_V + 0.0214 \left( \frac{T}{T_c} \right) C_p^{\circ 2}.$$

Here  $C_V$  = total heat capacity at constant volume for the compound at temperature  $T$  in cal  $^\circ\text{K}^{-1}$  gfw<sup>-1</sup>

$T$  = temperature in  $^\circ\text{K}$ ,

$T_c$  = melting point of compound in  $^\circ\text{K}$ , and

$C_p^\circ$  = total heat capacity at constant pressure in cal  $^\circ\text{K}^{-1}$  gfw<sup>-1</sup>

It is expected that the Nernst-Lindemann equation would be a better approximation at low temperatures, where  $C_p^\circ - C_V$  is small. As the temperature increases, the accuracy of the approximation must become less. Finally at a point where  $C_p^\circ = 2 C_V$ , the discriminant of the quadratic equation becomes negative. Thus, the upper-temperature limit for use of this equation occurs when

$$4(0.0214) \frac{\pi}{T_c} C_V = 1,$$

or

$$\frac{T}{T_c} = \frac{1}{4(0.0214) C_V}.$$

In using the above equation, the procedure followed by Krestovnikov and Vendrikh was used. That is, values of  $C_p^\circ$  per mole of compound were used. However, it would appear more appropriate to normalize values of  $C_p^\circ$  used, thus expressing  $C_p^\circ$  in cal/g atom. In this way, the high-temperature limit discussed above could be extended and the differences between  $C_p^\circ$  and  $C_V$  would be minimized as is to be expected.

Additional discussions of the Nernst-Lindemann equation have been made by Zemansky<sup>9</sup> and Partington.<sup>11</sup> The more extensive discussions of Partington<sup>11</sup> does not consider explicitly the use of the Nernst-Lindemann equation at high temperatures. Partington uses the equation with  $C_p^\circ$  and  $C_V$  defined as heat capacity per mole. He also mentions (p. 265) that  $C_p^\circ - C_V$  is only about 5 percent of  $C_p^\circ$  at the melting point for most solids. This would indicate that the proposed normalization discussed above is more appropriate. Reference to the original work of Nernst and Lindemann<sup>10</sup> shows that their equation had been based on 1 mole of particles; i. e.,  $6.02 \times 10^{23}$  atomic particles. Thus, their  $C_p^\circ$  and  $C_V$  refer to heat capacities per g atom rather than g mole.

In the present work, the Krestovnikov and Vendrikh procedure, utilizing the unnormalized Nernst-Lindemann relation, has been followed. To test the calculational procedures described, data were estimated for several carbides and borides. Density data for the elements were taken from Hansen and Anderko,<sup>12</sup> Melting-point data for the compounds investigated were, for the most part, also from Hansen and Anderko. Melting-point data for the elements were taken from the present or earlier reports.<sup>13</sup>

## 2. Borides and Carbides

In table 8, thermal data estimated at 298.15°K for several borides are shown. Similar data for several carbides are shown in table 9. In a few cases, other possible choices for melting points of the compound are shown in table 9. In general, it is not expected that a change of melting point chosen will be important unless the change is relatively large. In the case of HfC, a trial using a melting point of 4100°K, followed by a second trial at 3900°K, caused the entropy to increase by only about 0.3 cal °K<sup>-1</sup> gfw<sup>-1</sup> to the value tabulated; namely,

$$S_{298}^{\circ} = 9.852 \text{ cal } ^{\circ}\text{K}^{-1} \text{ gfw}^{-1} .$$

It is of some interest to compare experimental entropies and heat capacities with those calculated. A few comparisons are shown in tables 10 and 11.

From the data in table 11, it is seen that for ZrB<sub>2</sub>, it is not possible to make calculated  $S_{298.15}^{\circ}$  and  $C_{p298.15}^{\circ}$  values to agree simultaneously with the experimental values. A similar, but smaller, distinction is noticed for ZrC and TiC. Several factors might account for these distinctions; however, it should be again emphasized that the present calculations are dependent on empirical relationships. Also it is an oversimplification to assume that the Debye temperatures are a constant. It is well known that these characteristic temperatures vary with temperature. A normalized form of the Nernst-Lindemann equation as discussed earlier, or a better equation for  $C_p^{\circ} - C_v^{\circ}$ , might also give better agreement. For data between 0° and 298.15°K, it is not expected that normalization will cause entropy values ( $S_{298.15}^{\circ}$ ) to change more than a few tenths of an entropy unit (cal °K<sup>-1</sup> gfw<sup>-1</sup>). However, to go to very high temperatures, normalization will be more important.

Although the present calculations do have their limitations, it is worth noting their advantages. Thus, the estimates of entropy should probably be good to about  $\pm 0.5 \text{ cal } ^{\circ}\text{K}^{-1} \text{ g atom}^{-1}$ ; e.g., the estimated accuracy for a monoboride would be  $\pm 1.0 \text{ cal } ^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ , and for a diboride it would be  $\pm 1.5 \text{ cal } ^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ .

The estimates require a minimum of input data and do not require any auxiliary data as in the Latimer method.<sup>5</sup> Thus, the latter method requires a knowledge of the behavior of at least one member of the group.

TABLE 8

THERMAL DATA ESTIMATED AT 298.15°K FOR BORIDES

Compound	Melting Point	$\theta'$ Metal	$\theta'$ Nonmetal	$C_p^{\circ}$ <sub>298.15</sub>	$S^{\circ}$ <sub>298.15</sub>	$H^{\circ}$ <sub>298.15</sub> - $H^{\circ}$ <sub>0</sub>
	°K	°K	°K	cal°K <sup>-1</sup>	gfw <sup>-1</sup>	kcal gfw <sup>-1</sup>
CrB	1823	418.	1096.	8.989	8.140	1.410
CrB <sub>2</sub>	2123	451.	1183.	11.800	9.095	1.653
HfB <sub>2</sub>	3423	251.1	1503.1	10.290	11.068	1.706
MoB <sub>2</sub>	2523	332.	1290.	11.365	10.251	1.749
NbB <sub>2</sub>	3323	370.	1481.	10.166	8.931	1.524
TaB <sub>2</sub>	3473	270.	1514.	10.200	10.603	1.665
TiB <sub>2</sub>	3063	498.3	1421.9	10.152	7.516	1.381
VB <sub>2</sub>	2673	489.	1328.	10.729	7.973	1.465
ZrB <sub>2</sub>	3313	342.1	1478.3	10.241	9.380	1.569

TABLE 9

THERMAL DATA ESTIMATED AT 298.15°K FOR CARBIDES

Compound	Melting Point	$C_p^{\circ}, 298.15$	$S_{298.15}^{\circ}$	$H_{298.15}^{\circ} - H_0^{\circ}$
	$^{\circ}\text{K}$	$\text{cal } ^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$		$\text{kcal gfw}^{-1}$
HfC	3900	8.228	9.852	1.494
NbC	4073*	7.843	7.411	1.258
Nb <sub>2</sub> C	3353*	14.085	15.177	2.472
TaC	4073**	8.098	9.286	1.440
Ta <sub>2</sub> C	3773**	14.197	18.133	2.729
TiC	3523	7.787	6.185	1.126
VC	3103***	8.061	6.437	1.170
V <sub>2</sub> C	2950***	13.619	11.872	2.109
ZrC	3803	8.079	8.112	1.340

\*Storms<sup>14</sup> gives a melting point for NbC of about 3673°K and a peritectic decomposition of Nb<sub>2</sub>C at 3353°K.

\*\*Storms<sup>14</sup> gives a melting point for TaC of about 3983°K, but dropping rapidly, and a peritectic decomposition of Ta<sub>2</sub>C at 3673°K.

\*\*\*Storms<sup>14</sup> refers to a published work of Storms and McNeal<sup>15</sup> (1962) which indicates peritectic decompositions of VC at 2923°K and of V<sub>2</sub>C at 2438°K.

TABLE 10

COMPARISON OF  $S_{298.15}^{\circ}$  VALUES WITH OTHER DATA(All Values in cal $^{\circ}$ K $^{-1}$  gfw $^{-1}$ )

## Carbides

Compound	Present Calculations	Kelley <sup>16</sup>	Krikorian <sup>17</sup>	Other Sources
HfC	9.852	10.9(estd)	9.9 $\pm$ 0.5	
NbC	7.411	7.0 $\pm$ 0.5(estd)	8.6 $\pm$ 0.5	
Nb <sub>2</sub> C	15.177	---	18.4 $\pm$ 1.0	
TaC	9.286	10.11 $\pm$ 0.08	10.11 $\pm$ 0.08	
Ta <sub>2</sub> C	18.133	---	20.8 $\pm$ 1.0	
TiC	6.185	5.79 $\pm$ 0.05	5.79	
VC	6.437	6.77 $\pm$ 0.03	6.77 $\pm$ 0.03	
V <sub>2</sub> C	11.872	---	14.4 $\pm$ 1.0	
ZrC	8.112	9.3 $\pm$ 0.3(estd)	7.9 $\pm$ 0.5	7.964 <sup>a</sup>

## Borides and Miscellaneous

Compound	Present Calculations	Kelley <sup>16</sup>	Mezaki et al <sup>4</sup>	Other Sources
B	1.374			1.392 <sup>a</sup>
B <sub>4</sub> C	6.861	6.47		
CrB	8.140		8.7	
CrB <sub>2</sub>	9.095		6.6	
HfB <sub>2</sub>	11.068		11.2	
MoB <sub>2</sub>	10.251		8.7	
NbB <sub>2</sub>	8.931		8.6	
TaB <sub>2</sub>	10.603		11.3	
TiB <sub>2</sub>	7.516		6.2	
TiN	7.888	7.24		
TiO <sub>2</sub>	13.621	12.04		
VB <sub>2</sub>	7.973			
ZrB <sub>2</sub>	9.380			8.59 <sup>a</sup>

<sup>a</sup> Westrum.<sup>3</sup><sup>\*</sup> Present report.



TABLE 11

COMPARISON OF  $C_p^\circ$ , 298.15 VALUES FROM PRESENT CALCULATIONS  
WITH EXPERIMENTAL DATA

Compound	Method	$C_p^\circ$ , 298.15 cal °K <sup>-1</sup> gfw <sup>-1</sup>	$S_{298.15}^\circ$ gfw <sup>-1</sup>	$H_{298.15}^\circ - H_0^\circ$ kcal gfw <sup>-1</sup>
ZrB <sub>2</sub>	L. C. = 137*	10.241	9.38	1.569
	L. C. = 150	9.585	8.997	1.491
	L. C. = 160	9.140	8.760	1.441
	Westrum <sup>3</sup> Exptl.	11.53	8.586	1.590
ZrC	L. C. = 137	8.079	8.112	1.340
	Westrum Exptl.	9.058	7.964	1.401
TiC	L. C. = 137	7.787	6.185	1.126
	Kelley <sup>16</sup> Exptl.	8.04	5.79	---

\*L. C. = Lindemann Constant.

### 3. Nitrides

The preceding work has been devoted primarily to the estimation of low-temperature heat capacities and entropies for borides and carbides. Next, it is important to consider the transition metal nitrides.

The results of the calculations for a group of nitrides are summarized in table 12. Most of the melting points have been taken from Hansen and Anderko,<sup>12</sup> and Storms.<sup>18</sup>

TABLE 12

THERMAL DATA ESTIMATED AT 298.15°K FOR NITRIDES

Compound	Melting Point (°K)	$C_p^\circ, 298.15$	$S_{298.15}^\circ$	$H_{298.15}^\circ - H_0^\circ$ (kcal gfw <sup>-1</sup> )
		(cal deg K <sup>-1</sup> gfw <sup>-1</sup> )		
TiN	3223 <sup>a</sup>	9.378	7.888	1.425
ZrN	3253 <sup>a</sup>	9.803	10.108	1.671
HfN	3583 <sup>a</sup>	9.794	11.487	1.773
Nb <sub>2</sub> N	2673 <sup>b</sup>	16.13	18.339	2.938
NbN	2323 <sup>b</sup>	10.421	11.391	1.846
TaN	3363 <sup>b</sup>	9.888	11.412	1.779
Ta <sub>2</sub> N	3000 <sup>c</sup>	16.205	21.245	3.163

Notes:

a Hansen and Anderko.<sup>12</sup>

b Storms.<sup>18</sup>

c Estimated roughly.

In the case of the TiN and ZrN data, Kelley and King<sup>16</sup> tabulate experimental values of  $S_{298.15}^\circ = 7.24$  e.u. and 9.29 e.u. It is thus seen that the estimation procedure gives reasonable values. In cases where good experimental values are available, naturally the experimental data are preferable. However, for many of the nitrides for which low-temperature data are missing, the present data should be moderately good.

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## E. MISCELLANEOUS

### 1. The Functions $\Delta H_f^\circ$ , $\Delta F_f^\circ$ , and $\log_{10} K_p$

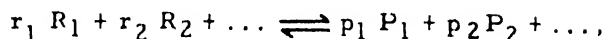
A set of equations which finds repeated use in calculations of the three functions,  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$ , is

$$\Delta H_f^\circ = \Delta H_{f298}^\circ + \Delta(H_T^\circ - H_{298}^\circ) \quad , \quad (\text{III E1-1})$$

$$\Delta F_f^\circ = \Delta H_{f298}^\circ - T\Delta(f.e.f.) \quad , \quad (\text{III E1-2})$$

$$\log_{10} K_p = \frac{-\Delta F_f^\circ}{4.575835 T} \quad . \quad (\text{III E1-3})$$

If the chemical equation is given as



then

$$\Delta(f.e.f.) = \Delta \left[ - \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right] \\ = \sum_{\text{products}} p_i \left[ - \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right]_i - \sum_{\text{reactants}} r_i \left[ - \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) \right]_i \quad . \quad (\text{III E1-4})$$

### 2. Calculation of Uncertainty in Entropy of Transition

For phase changes where one has given  $\Delta H \pm \delta\Delta H$  and  $T \pm \delta T$ , one can write equations (III E2-1) and (III E2-2) to represent the entropy change and its uncertainty  $\delta\Delta S$ .

$$\Delta S \pm \delta\Delta S = \frac{\Delta H \pm \delta\Delta H}{T \pm \delta T} \quad (\text{III E2-1})$$

$$= \frac{\Delta H}{T} \pm \frac{\delta\Delta H}{T} \mp \frac{\Delta H \delta T}{T(T \pm \delta T)} \mp \frac{\Delta H \delta T}{T(T \pm \delta T)} \quad . \quad (\text{III E2-2})$$

Picking the combination of signs for  $\delta\Delta H$  and  $\delta T$  which leads to the largest value of  $\delta\Delta S$  yields equation (III E2-3) for the uncertainty in the entropy of the transition.

$$\delta\Delta S = \frac{\delta\Delta H}{T} + \frac{(\Delta H + \delta\Delta H)\delta T}{T(T - \delta T)} \quad . \quad (\text{III E2-3})$$

### 3. The Boiling Point

A special procedure was adopted for the handling of boiling-point entries in thermodynamic tables to maintain consistency.

At the normal boiling point, the entropy of the ideal gas is exactly equal to the sum of the integrated  $C_p^\circ/T$  functions of the solid and liquid and the entropies of fusion and vaporization. This consistency is only maintained if the boiling point is taken exactly at the temperature where  $\Delta F_T^\circ$  changes sign in the ideal gas table. It has been found from experience that carrying the boiling point to two decimal places is sufficient for agreement in the thermodynamic functions to three decimal places, and boiling points have been recorded to two decimal places routinely in the tables even though this does not represent the real accuracy of the value.

The calculated boiling point will not necessarily correspond to values determined elsewhere, and if the basic data are good, the agreement with other reported values should be reasonably good. The boiling points otherwise reported in the present compilation are the calculated values rounded off to the nearest degree. This rounded-off value is used everywhere except in the table entry. The detailed data reviews must be consulted for the other reported values of boiling points.

#### IV. DATA REVIEWS AND COMPUTATION SUMMARIES FOR INDIVIDUAL ELEMENTS AND COMPOUNDS

##### A. ELEMENTS

###### 1. Beryllium

The Reference State and Ideal Monatomic Gas Tables for beryllium presented in the first technical summary report<sup>1</sup> were modified to include the recent high-temperature heat-content measurements of Kantor, Krasovitskaya, and Kisel<sup>2</sup> (600° to 2200°K). Although the changes introduced are small, the new data are based on the first experimental measurement of the heat of fusion of beryllium and of the heat capacity of the liquid. The assigned uncertainties were accordingly modified. All tables relating to beryllium and its compounds reported herein are intended to supersede corresponding tables that had been previously reported. Data from the previous summary<sup>1</sup> were used except as indicated here.

The results of Kantor, Krasovitskaya, and Kisel<sup>2</sup> in cal/gfw over the temperature range from 600° to 2200°K were summarized by the expressions

$$H_T^\circ - H_{298.16}^\circ = 4.322T + 1.09 \times 10^{-3}T^2 - 1490 \quad , \quad (\text{IVA1-1})$$

for the temperature range from 600° to 1560°K; and

$$H_T^\circ - H_{298.16}^\circ = 6.079T + 2.569 \times 10^{-4}T^2 + 1327 \quad , \quad (\text{IVA1-2})$$

for the temperature range from 1560° to 2200°K.

They reported the melting point to be  $1560^\circ \pm 5^\circ\text{K}$  and the heat of fusion to be  $3.520 \pm 0.080$  Kcal/gfw. The heat of fusion of beryllium had been previously estimated to be  $2.800 \pm 0.500$  Kcal/gfw. The plot presented of their experimental data did not show a separate heat-content discontinuity just below the melting point corresponding to a heat of transition for a hcp-bcc\* transformation. However, the existence of such a transformation, 15° to 20° below the melting point, is quite likely; and the heat of fusion reported by them probably included a heat of solid-state transformation. The previously accepted value of the m.p. equal to  $1556^\circ \pm 3^\circ\text{K}$  was retained in the new tables.  $\Delta S_m^\circ$  was, therefore,  $2.262 \pm 0.055$  e.u.

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\*That is, hexagonal close-packed and body-centered cubic.

Between 600° and 1200°K, the heat-content data of Kantor, Krasovitskaya, and Kisel<sup>2</sup> agreed with those of Ginnings, Douglas, and Ball<sup>3</sup> within  $\pm 4$  cal/gfw. The latter were used for the previous Reference State Table.<sup>1</sup> Between 1100°K and the melting point, the heat capacity, as given by the newer data, was slightly lower than that from the previously adopted extrapolation of the data of Ginnings, Douglas, and Ball.<sup>3</sup>

The liquid heat-capacity data of Kantor, Krasovitskaya, and Kisel<sup>2</sup> were extrapolated to the boiling point. The liquid heat capacity had been previously estimated to be 7.500 cal/°K gfw.

The normal boiling point was changed from  $2754^\circ \pm 50^\circ$  to  $2767.61^\circ \pm 35^\circ$ K. The heat of vaporization at the normal boiling point was consequently found to be  $70.169 \pm 0.870$  Kcal/gfw, and the corresponding entropy of vaporization was  $25.336 \pm 0.329$  e.u. Values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log K_p^\circ$  were also revised.

High-temperature heat capacities of beryllium were also reported by Mitkina.<sup>4</sup> The novel method of measurement used, however, gave results in marked disagreement with the values adopted herein.

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## 2. Boron

In an earlier report,<sup>1</sup> tables for the boron reference state and the ideal gas state were presented. Because additional data have been published for these states, it was considered desirable to review all of the new data.

### a. Condensed Phases

New heat-capacity data were reported by McDonald and Stull<sup>2</sup> for boron from 298.15° to 1700°K. Their data had been fitted with a Shomate function and  $C_p^{\circ}{}_{298.15} = 2.67 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . The equation that they reported was

$$C_p^{\circ} = 4.735 + 1.38 \times 10^{-3}T - 2.201 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1} \quad (\text{IVA2-1})$$

A calculation of a condensed phase table for boron was then made using  $S_{298.15}^{\circ} = 1.42 \text{ e. u.}$ , based on the work of Johnston, Hersh, and Kerr.<sup>3</sup> Comparison of the resulting data with the data from the earlier report<sup>1</sup> showed very good agreement. Free-energy functions from the earlier report were larger than the new data by only 0.05 e. u. at 2400°K for a percentage difference of only 0.6 percent. This difference is equivalent to only  $0.05 \times 2400 = 120 \text{ cal}$ , which is negligibly small compared to the accuracy of vaporization data for boron. In view of the good agreement, it was considered reasonable to retain the earlier condensed phase data for boron.

### b. Vaporization Data

Recent years have seen considerable effort expended on obtaining the vapor-pressure data pertinent to elemental boron. Work not already reported<sup>1</sup> includes the works of Alcock and Grieson,<sup>4</sup> Priselkov et al.,<sup>5</sup> Hildenbrand et al.,<sup>6</sup> Kibler et al.,<sup>7</sup> Goldstein and Trulson,<sup>8</sup> and Verhaegen and Drowart.<sup>9</sup>

The work thus far reported continues to yield a relatively large scatter. There is still a discrepancy between the data, in that mass spectrometric determinations tend to give a higher effective vapor pressure, whereas weight-loss methods give lower vapor pressures.

Alcock and Grieson<sup>4</sup> by a weight-loss method found vapor pressures in general agreement with Searcy and Myers' data.<sup>10</sup> Similarly, Hildenbrand et al.<sup>6</sup> by torsion effusion reported  $\Delta H_{298}^{\circ} = 136.1 \text{ kcal/mole}$ . Their data were also confirmed by boron carbide decomposition.



The mass spectrometric determinations of Verhaegen and Drowart<sup>9</sup> yield  $\Delta H_0^\circ = 128 \pm 2.5$  kcal/mole which, when recalculated, gives  $\Delta H_{298}^\circ = 129.221$  kcal/mole. This is in excellent agreement with data obtained at Union Carbide Laboratories by Goldstein and Trulson.<sup>8</sup> The last workers performed new experiments on the mass spectrometer in excellent agreement with the earlier work of Schissel and Williams<sup>11</sup> at the same laboratories. They had found  $\Delta H_{298}^\circ = 129.0$  kcal/mole.

Priselkov et al<sup>5</sup> found unusually high-vapor pressures, and hence their data are not further considered. Kibler et al<sup>7</sup> reported initial experiments to use resonance atomic absorption. However, they had not yet performed definitive experiments.

Thus, at this time, there appear to be two schools of thought; i. e., (1) mass-spectrometry data yield  $\Delta H_{298}^\circ$  values of about 129 to 130 kcal/mole whereas, (2) the weight-loss methods yield values of about 136 kcal/mole.

In view of this discrepancy, which could not be resolved at a recent boride symposium at the A. D. Little Laboratories, it is felt advisable to continue using the average value of  $\Delta H_{298}^\circ = 133$  kcal/mole adopted earlier.<sup>1</sup> It is clear that this value is subject to an uncertainty, which seems to be about  $\pm 4$  kcal/mole.

#### c. Recompilation of Reference State Table and Ideal Monatomic Gas Table

In the original tables,<sup>1</sup> a metastable reference state above the boiling point was chosen for boron. For the purposes of being more compatible with other tables already presented, it was felt advisable to use the more conventional reference table having a normal boiling point and a gas phase above the boiling point. Hence the two tables; i. e., reference state and monatomic gas tables, were recompiled using the same basic data as used earlier.<sup>1</sup> A boiling point of 3969.96°K was found.

#### Supplement

Langmuir vaporization data have been reported by Paule and Margrave.<sup>12</sup> Vaporization of boron in an arc has been studied by Kathavate and Rihani.<sup>13</sup> Tavazze et al<sup>14</sup> have studied the density and surface tension of molten boron. Gorski<sup>15</sup> has reported a new orthorhombic form of boron.

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### 3. Calcium

For a discussion of this element, see Barriault, R. J. et al, *Thermodynamics of Certain Refractory Compounds*, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this report.

### 4. Carbon

#### a. Graphite

Recent compilations of the thermodynamic functions of graphite are those of Evans<sup>1</sup> (up to 4000°K) and of Stull and co-workers<sup>2</sup> (an extrapolation of the work of Evans up to 6000°K). These compilations were accepted in the present work.

The entropy and enthalpy values at 298.15°K ( $S_{298}^0 = 1.359$  e.u. and  $H_{298}^0 - H_0^0 = 252$  cal/gfw) of Evans<sup>3</sup> are based on the heat-capacity data of DeSorbo and Tyler.<sup>4</sup> Above 298.15° to 2000°K, Evans<sup>3</sup> used the enthalpy data of Magnus.<sup>5</sup> Terres and Schaller,<sup>6</sup> Weber,<sup>7</sup> and Lucks and Deem,<sup>8</sup> and the heat-capacity data of Worthing.<sup>9</sup> These data were then combined with the compressibility and thermal expansion data of Day and Sosman,<sup>10</sup> to estimate an average value of the Debye  $\theta$ . This average Debye  $\theta$  was then used from 2000° to 4000°K.

It should be noted that this compilation ignores the experimental heat-capacity values above 3000°K reported by Rasor and McClelland.<sup>11</sup> The data of Rasor and McClelland<sup>11</sup> indicate a very sharp rise in the  $C_p^0$  versus  $T$  curve at about 3600°K, and inclusion of their data would appreciably alter existing compilations. Although rises in  $C_p^0$  just below the m.p., supposedly a premelting phenomenon, have been reported in some solids, it appears unlikely that such a sharp rise is valid for carbon. Rasor and McClelland<sup>11</sup> fitted the excess specific heat to an exponential expression of the form expected for the number of defects (i.e., proportional to  $e^{-E/kT}$ ) and obtained an energy of defect formation  $E$  approximately equal to the heat of vaporization of carbon. Friedel<sup>12</sup> has pointed out in connection with his analysis of uranium  $C_p^0$  data, however, that the correct expression for the defect formation contribution to specific heat should be proportional to  $(1/T^2)e^{-E/kT}$ . The use of Friedel's formula with Rasor and McClelland's data<sup>11</sup> would result in a larger (and undoubtedly variable) value of  $E$  that would be difficult to justify.

Since graphite is an electrical conductor, appreciable electronic contributions should be expected at very high temperatures. Estimates of this effect have not been included in available tabulations.

### b. Monatomic Gas (C)

Thermodynamic functions for the ideal monatomic gas were calculated using all the spectroscopic energy levels listed by Moore.<sup>13</sup> Energy levels and J values not definitely established in these tables were estimated.

The standard heat of sublimation of graphite to monatomic carbon vapor,  $\Delta H_{s298}^{\circ}$ , has been the subject of considerably disagreement over a period of several years but is now generally accepted as being  $170.890 \pm 0.450$  Kcal/gfw.<sup>2, 14-16</sup>  $H_{298}^{\circ} - H_0^{\circ}$  for monatomic carbon vapor was calculated to be 1562 cal/gfw.

The monatomic gas table was computed even though other tables exist, to be consistent with the other monatomic gas tables in this compilation since all available energy levels were used in the present work.

### c. Diatomic Gas (C<sub>2</sub>)

The thermodynamic properties of C<sub>2</sub> gas have also been the subject of some disagreement for several years.<sup>17-19</sup> The dispute has centered about the location and number of electronic states, and in particular the characterization of the ground state. The work of Ballik and Ramsay<sup>20, 21</sup> is now accepted, thus firmly establishing the  $1\Sigma^+$  state as the ground state for the C<sub>2</sub> molecule. Altman<sup>19</sup> has recently calculated the thermodynamic functions of C<sub>2</sub> gas up to 5000°K based on the observed spectroscopic constants of Ballik and Ramsay.<sup>20, 21</sup> More recently, Clementi<sup>22</sup> has predicted the existence, location, and spectroscopic constants for several additional electronic states and has recalculated the thermodynamic functions for C<sub>2</sub> gas from 2000° to 6000°K, taking into account all experimentally observed and estimated electronic states. The thermodynamic functions for C<sub>2</sub> gas in the present compilation were calculated with all the spectroscopic constants of Clementi.<sup>22</sup> The spectroscopic constants employed (in cm<sup>-1</sup> units) are summarized in table 13.

The mass spectrographic data of Drowart and co workers,<sup>16</sup> combined with the free-energy functions for graphite and C<sub>2</sub> gas given herein, lead to a value of  $\Delta H_{s298}^{\circ}$  for the formation of C<sub>2</sub> gas from graphite of  $198.660 \pm 2.000$  Kcal/gfw. This is in rather good agreement with the average value from all mass spectrometer and King furnace data of  $\Delta H_{s0}^{\circ} = 195 \pm 5$  Kcal/gfw recently reported by Brewer et al,<sup>23</sup> which corresponds to  $\Delta H_{s298}^{\circ} = 197 \pm 5$  Kcal/gfw. The value of 199.0 Kcal/gfw used by the JANAF compilation, therefore, appears to be slightly high. The value of  $H_{298}^{\circ} - H_0^{\circ}$  for C<sub>2</sub> was calculated to be 2528 cal/gfw.

TABLE 13

THE SPECTROSCOPIC CONSTANTS OF GASEOUS C<sub>2</sub> (cm<sup>-1</sup>)

E	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$B_e$	$a_e$	$\gamma_e$	$D_e (\times 10^6)$	$g^*$
0.00	1853.91	13.33	-0.17	1.81829	0.01763	-0.00023	7.35	1
610.00	1640.64	11.66	0.0	1.6312	0.01636	0	7.01	6
8268.30	1607.64	12.068	-0.01	1.61496	0.01684	-0.00005	6.34	2
6243.40	1469.81	11.18	0.02	1.49724	0.01632	0	6.21	3
10000.00	1481.0	11.14	0	1.486	0.015	0	5.98	2
14000.00	1470.0	10.06	0	1.475	0.013	0	5.94	1
14300.00	1891.0	14.23	0	1.897	0.018	0	7.64	3
19988.40	1787.45	16.43	-0.5061	1.7512	0.01606	0	6.72	6
34237.66	1808.3	15.80	-4.01	1.7319	0.01798	0	6.8	2
40000.00	1259.0	9.48	0	1.264	0.012	0	5.10	3
40000.00	1261.0	9.89	0	1.266	0.012	0	5.10	1
40416.26	1106.08	39.23	2.801	1.1912	0.0242	0	6.3	6
43227.21	1828.78	13.96	0	1.8318	0.204	0	7.88	1

\*g is dimensionless

d. Triatomic Gas (C<sub>3</sub>)

Available spectroscopic constants for C<sub>3</sub> gas are at present estimated rather than experimentally determined values. The work of Engelke<sup>24</sup> offers further evidence that the <sup>1</sup>Σ state is the ground-state of C<sub>3</sub> as indicated by Thorn and Winslow.<sup>25</sup> The fundamental frequencies were estimated by Pitzer and Clementi,<sup>18</sup> by analogy to the allene molecule. It should be noted that the frequencies estimated by Pitzer and Clementi are somewhat higher than those estimated earlier by Glockler.<sup>26</sup> The thermodynamic properties of C<sub>3</sub> given in the table presented herein were calculated with the following input data.

$$\text{C-C bond distance} = 1.281\overset{\circ}{\text{\AA}},$$

$$\text{Moment of inertia} = 65.448 \times 10^{-40} \text{ g cm}^2,$$

$$\text{Symmetry number} = 2,$$

$$\omega_1 = 1300 \text{ cm}^{-1},$$

$$\omega_2 = 550 \text{ cm}^{-1} \text{ (multiplicity} = 2\text{)}$$

$$\omega_3 = 2200 \text{ cm}^{-1},$$

$$\text{Ground electronic state} = {}^1\Sigma.$$

The mass spectrographic data of Drowart and co-workers,<sup>16</sup> combined with the free-energy functions for graphite and C<sub>3</sub> gas given in the table presented herein, lead to a value of  $\Delta H_{f298}^\circ$  for the formation of C<sub>3</sub> gas from graphite of  $188.940 \pm 3.000$  Kcal/gfw. This is slightly different from the value in the JANAF compilation.<sup>2</sup> Brewer and Engelke<sup>27</sup> have recommended a value of  $\Delta H_0^\circ = 188 \pm 5$  Kcal/gfw on the basis of their spectral analysis of C<sub>3</sub>. This corresponds to  $\Delta H_{f298}^\circ = 187.6 \pm 5$  Kcal/gfw. All values of  $\Delta H_{f298}^\circ$  agree within the experimental error. The value calculated in the present work was chosen for the present compilation to preserve the consistency and uniformity within this compilation. The value of  $H_{298}^\circ - H_0^\circ$  for C<sub>3</sub> gas was calculated to be 2319 cal/gfw.

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## 5. Cerium

### a. Crystal Structure, Transition Points, and Melting Point

The description of the allotropy of elemental cerium near room temperature and below was found to be complicated by slow rates of the transformations, and hence, by the occurrence of metastable phases. In this range of temperature, two or more modifications might be observed simultaneously in proportions and over temperature ranges which would depend on the thermal and mechanical history of the metal as well as on the presence of small amounts of impurities. McHargue and Yakel<sup>1</sup> recently studied the conditions under which the various allotropic modifications appeared, and their article could be consulted for references to earlier work on the subject.

In general, however, a face-centered cubic form,  $\gamma$ -Ce,\* has been considered to be thermodynamically stable between 1003° and about 260°K.<sup>1,2</sup> Crystallographic data for this phase have been given by Spedding, Daane, and Hermann.<sup>3</sup> Between about 260° and about 150°K, the stable form has usually been considered to be hexagonal close-packed  $\beta$ -Ce,<sup>1,2</sup> although Dialer and Rothe<sup>4</sup> have reported both  $\beta$ -Ce and  $\gamma$ -Ce to be face-centered cubic.

To complicate the picture still further, Weiner and Raynor<sup>5</sup> were unable to produce a transformation from  $\gamma$ -Ce to  $\beta$ -Ce, and they observed a possible additional face-centered cubic phase. This latter phase, designated by them as  $\gamma'$ -Ce, was observed after annealing  $\gamma$ -Ce for long periods of time above 500°C followed by slow cooling. It was stated, however, that the phase might have been due to small amounts of hydrogen in their sample.

Pure  $\beta$ -Ce had never been reported. Crystallographic data for  $\beta$ -Ce was given by McHargue, Yakel, and Jetter<sup>6</sup> and by McHargue and Yakel.<sup>1</sup> Commercial cerium had been considered to contain sufficient calcium and magnesium to inhibit the formation of  $\gamma$ -Ce from  $\beta$ -Ce.<sup>7</sup>

Below about 150°K, a dense, or "collapsed," face-centered cubic phase,  $\alpha$ -Ce, had been considered to be the stable form.<sup>1,2</sup> It had been suggested that the appearance of  $\alpha$ -Ce would mark the movement of the one 4f electron in cerium to the conduction band.<sup>8,9</sup> This interpretation was consistent with the neutron diffraction studies on metallic cerium by Wilkinson and others.<sup>10</sup> Crystallographic data for  $\alpha$ -Ce were given by Lawson and Tang,<sup>8</sup> and by Schuch and Sturdivant.<sup>11</sup> High-pressure

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\*Various authors have adopted different symbols to designate the allotropic modifications of cerium.



studies on cerium<sup>12-16</sup> showed a high-pressure, room-temperature, face-centered cubic phase to be identical with  $\alpha$ -Ce. Results of the high-pressure studies were used to arrive at an estimate of  $S_{298}^0$  for cerium.

Cerium had been reported to exhibit a further heat-capacity anomaly at 12.5°K.<sup>17,18</sup> An anomaly at that temperature was also detected in susceptibility measurements.<sup>19</sup> Lock suggested that this anomaly was due to antiferromagnetic ordering, presumably in  $\gamma$ -Ce. Parkinson, Simon, and Spedding<sup>17</sup> made an alternate suggestion that this behavior was due to excitation of electrons between energy levels produced by Stark splitting of the ground state. Parkinson and Roberts<sup>18</sup> concluded that the anomaly would occur if 4f electrons were present in the metal; i. e., in  $\beta$ - or  $\gamma$ -Ce. Wilkinson and others,<sup>10</sup> from their neutron diffraction studies, concluded that the anomaly at 12.5°K was due to antiferromagnetic ordering, and that it occurred in hexagonal close-packed  $\beta$ -Ce. It might be added that it would be possible to study virtually pure  $\alpha$ -Ce (i. e., in the absence of significant amounts of  $\gamma$ -Ce) and establish some features of an  $\alpha$ - $\gamma$  transition well below the temperature at which  $\gamma$ -Ce would be believed to be thermodynamically stable.

Cerium containing a mixture of phases at room temperature had been reported to become single-phased  $\gamma$ -Ce when heated to about 420°K.<sup>1</sup> At 1003°  $\pm$  5°K,<sup>20,21</sup>  $\gamma$ -Ce had been reported to transform rapidly and reversibly to body-centered cubic  $\delta$ -Ce;<sup>20</sup> i. e., the stable form at temperatures up to the melting point. Prior to the electrical resistivity measurements<sup>22</sup> which established the  $\gamma$ - $\delta$  transition temperature as 1003°K, thermal analysis studies gave this transition as 1027°K.<sup>23</sup> Heat-content measurements on  $\delta$ -Ce at 1016°K by Spedding, McKeown, and Daane<sup>23</sup> supported the lower transition temperature. This transition temperature should be accepted in preference to the pair of high-temperature transition temperatures tabulated by NBS Circular 500<sup>24</sup> from the work of Jaeger and Rosenbohm,<sup>25</sup> and that of Jaeger, Bottema, and Rosenbohm.<sup>26,27</sup> Crystallographic data for  $\delta$ -Ce were given by Spedding, Hanak, and Daane.<sup>20</sup>

## b. Thermodynamic Properties

### 1) Heats of transition and fusion

The heat of the  $\gamma$ - $\delta$  transition in cerium was measured by Spedding, McKeown, and Daane<sup>23</sup> and found to be 700  $\pm$  8 cal/gfw at 1003°K. This gave an entropy of transition of 0.698  $\pm$  0.008 e. u. They also found the heat of fusion of cerium to be 1238  $\pm$  4 cal/gfw at 1077°K; this corresponded to an entropy of fusion of 1.149  $\pm$  0.004 e. u. Thus, the entropy of the f. c. c. -b. c. c. transition plus the entropy of fusion were altogether 1.847  $\pm$  0.012 e. u.

## 2) Entropy and heat content at 298.15°K

The low-temperature (1.5° to 200°K) heat capacity of cerium was measured by Parkinson, Simon, and Spedding,<sup>17</sup> Simon and Ruhemann,<sup>28</sup> and Parkinson and Roberts.<sup>18</sup> Parkinson, Simon, and Spedding<sup>17</sup> made measurements on two samples of cerium. One sample was stated to contain only  $\gamma$ -Ce at room temperature although its structure at the various measurement temperatures was unknown and was doubtless complicated. A second sample contained a mixture of  $\beta$ -Ce and  $\gamma$ -Ce. Kelley and King<sup>29</sup> adopted the heat-capacity results obtained on the first sample and extrapolated them to obtain a value of 7.02 cal/°K gfw at 298.15°K. They reported  $S_{298}^{\circ}$  to be  $16.6 \pm 1.0$  e.u. This was the value of  $S_{298}^{\circ}$  tabulated by Parkinson, Simon, and Spedding<sup>17</sup> for  $\gamma$ -Ce from their heat-capacity measurements after adding 0.35 e.u. to correct for the effect of the  $\alpha$ -Ce present on the entropy of the transition at 12.5°K. The results of Parkinson and Roberts,<sup>18</sup> from studies on  $\gamma$ -Ce between 1.5° and 20°K, suggested that a further correction of 0.16 e.u. should be made to give a true value of 16.8 e.u. for the  $S_{298}^{\circ}$  of  $\gamma$ -Ce.

There was considerable uncertainty as to the phase composition of the cerium during most of the above-described measurements. The heat capacity of 6.90 cal/°K gfw at 200°K was considerably larger than the value of 6.440 cal/°K gfw at 298.15°K from the high-temperature measurements of Spedding, McKeown, and Daane.<sup>23</sup> Therefore,  $S_{298}^{\circ}$  was herein estimated as the sum of a lattice vibration contribution from an adopted Debye characteristic temperature, a contribution from the electronic heat capacity and  $C_p - C_v$ , and a contribution from an  $\alpha$ - $\gamma$  transition taken to occur at 150°K.

The Debye characteristic temperature of  $\gamma$ -Ce from the results of Parkinson, Simon, and Spedding,<sup>17</sup> obtained from studies at temperatures between 20° and 40°K, was  $115 \pm 2^{\circ}\text{K}$ . This value of  $\theta_D$  was supported by the results of measurements by Parkinson and Roberts<sup>18</sup> on  $\gamma$ -Ce near 20°K. It was used for the estimates of lattice vibration contributions to  $S_{298}^{\circ}$  and  $H_{298}^{\circ} - H_0^{\circ}$ . These contributions were 13.650 e.u. and 1.534 kcal/gfw, respectively. The estimated lattice specific heat at 298.15°K was 5.918 cal/°K gfw. The combined contribution of electronic specific heat and  $C_p - C_v$  was estimated to be proportional to the absolute temperature and to be equal, at 298.15°K, to the difference between the adopted  $C_p^{\circ}$  and the lattice specific heat, or 0.520 cal/°K gfw. The resulting contributions to  $S_{298}^{\circ}$  and  $H_{298}^{\circ} - H_0^{\circ}$  were 0.520 e.u. and 0.078 kcal/gfw, respectively.

The high-pressure studies of Poniatovskii,<sup>13</sup> Likhter, Riabinin, and Vereshchagin,<sup>16</sup> Herman and Swenson,<sup>14</sup> and Beecroft and Swenson<sup>15</sup> showed that the  $\alpha$ - $\gamma$  phase transformation varied linearly with pressure and that  $dP/dT = 43 \pm 2$  atm/°K. The data could be extrapolated to a transition temperature of  $150^\circ \pm 20^\circ\text{K}$  at 1 atm pressure. From X-ray measurements, Lawson and Tang<sup>8</sup> and Schuch and Sturdivant<sup>11</sup> reported  $\Delta V/V_0$  for this transition to be 0.165 at atmospheric pressure. The molar volume of cerium was taken to be  $20.2\text{ cm}^3$ . The Clausius-Clapeyron equation was used with these data to calculate an entropy of transition of 3.470 e.u. and a heat of transition of 0.521 kcal/gfw at  $150^\circ\text{K}$ . Thus, the adopted value of  $S_{298}^\circ$  became 17.640 e.u. and that of  $H_{298}^\circ - H_0^\circ$  was 2.133 kcal/gfw. An uncertainty of  $\pm 0.800$  e.u. was assigned to the entropy.

Jennings<sup>30</sup> used a similar procedure to estimate  $S_{298}^\circ$  to be 18.12 e.u., a value which was adopted by Spedding, McKeown, and Daane.<sup>23</sup> Hultgren and others<sup>31</sup> similarly estimated  $S_{298}^\circ$  to be  $15.3 \pm 2$  e.u. From a comparison of the values of  $S_{298}^\circ$  for the various rare earths for which there were the most reliable experimental data,<sup>29</sup> a value of 18.0 e.u. appeared to be reasonable.

### 3) High-temperature heat content

The high-temperature heat-content measurements of Spedding, McKeown, and Daane<sup>23</sup> superseded the earlier measurements of Jaeger and Rosenbohm,<sup>25</sup> and those of Jaeger, Bottema, and Rosenbohm,<sup>26, 27</sup> on which the compilations of Kelley<sup>32</sup> and Stull and Sinke<sup>33</sup> were based. The results of Spedding, McKeown, and Daane (with  $C_p^\circ$  in cal/°K gfw)<sup>23</sup> could be represented over the temperature range of  $298^\circ$  to  $1400^\circ\text{K}$  by the following equations:

$$C_p^\circ(\gamma) = 5.649 + 2.300 \times 10^{-3} T + 11.862 \times 10^{-7} T^2, \quad (\text{IVA5-1})$$

$$C_p^\circ(\delta) = 9.047 \text{ cal/}^\circ\text{K gfw.} \quad (\text{IVA5-2})$$

$$C_p^\circ(\text{liq.}) = 9.345 \text{ cal/}^\circ\text{K gfw.} \quad (\text{IVA5-3})$$

$$\Delta H^\circ(\gamma - \delta)_{1003^\circ} = 0.700 \pm 0.008 \text{ kcal/gfw.} \quad (\text{IVA5-4})$$

$$\Delta H^\circ(\delta - \text{liq.})_{1077^\circ} = 1.238 \pm 0.004 \text{ kcal/gfw.} \quad (\text{IVA5-5})$$

The above value of the heat capacity of liquid cerium was adopted for use up to the boiling point.

#### 4) Ideal monatomic gas

It was not possible to calculate the ideal monatomic gas thermodynamic functions of cerium from its energy levels as the latter had not been tabulated. For purposes of the present compilation, the energy levels of cerium gas were assumed to be identical to those of lanthanum as listed by Moore.<sup>34</sup>

#### 5) Standard heat of formation of the gas and the boiling point

The vapor pressure of cerium was measured by Brewer,<sup>35</sup> Ahmann,<sup>36</sup> Daane and Spedding,<sup>37</sup> and Gilles and Jackson.<sup>38</sup> The data of the last authors were not available. However, Spedding and Daane<sup>2</sup> reported that the heat of vaporization from the data of Gilles and Jackson<sup>38</sup> was somewhat higher than the value reported by Ahmann,<sup>36</sup> and Daane and Spedding.<sup>37</sup> Ahmann<sup>36</sup> represented his data by the equation

$$\log P_{\text{mm}} = \frac{-23400 \pm 440}{T} + 11.58 \pm 0.27, \quad (\text{IVA5-6})$$

and Daane and Spedding<sup>37</sup> represented their data by the equation

$$\log P_{\text{mm}} = \frac{-20304 \pm 81}{T} + 8.3062 \pm 0.0447. \quad (\text{IVA5-7})$$

The results of the first three authors<sup>35-37</sup> were in wide disagreement but bracketed  $\Delta H_s^\circ$  at 298.15°K between 80 and 111 kcal/gfw. The agreement between calculations of  $\Delta H_{f298}^\circ$  by Second- and Third-Law methods was also very poor. However, because of the assumption made in calculating the thermodynamic functions for monatomic cerium gas, this comparison should not be pushed too far. Spedding and Daane<sup>2</sup> recommended a value of 95 kcal/gfw for  $\Delta H_{f298}^\circ$ , and the same value could be estimated from a comparison of that quantity for other rare-earth metals.<sup>2, 39, 40</sup> This value was adopted herein, and an uncertainty of  $\pm 2.500$  kcal/gfw was assigned to it.

The normal boiling point of cerium was calculated to be 4270.73°  $\pm$  490°K. This boiling point was considerably higher than the value of 3200°K given by Stull and Sinke<sup>33</sup> and of 3742°K given by Hultgren and others.<sup>31</sup> The increase in the normal boiling point was due to the attempt to include a contribution from the energy levels of cerium gas to its thermodynamic functions and/or the adoption of a larger  $\Delta H_s^\circ$  value at 298.15°K.

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## 6. Chromium

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.

## 7. Dysprosium

An analysis of thermochemical data for dysprosium was not initiated during this project; however, a bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.

## 8. Gadolinium

An analysis of thermochemical data for gadolinium was not initiated during this project; however, a bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.



## 9. Hafnium

In an earlier report,<sup>1</sup> reference state and monatomic gas tables were presented. New heat-capacity and vaporization data indicated the necessity for revision of both tables.

No experimental high-temperature heat-capacity data had been available for the earlier tabulation. Recent work for pure hafnium by Fieldhouse and Lang<sup>2</sup> covered the range of 501° to 2931°F (533° to 1883°K). Their corrected equation<sup>3</sup> was

$$C_p^\circ = 0.0378 + 0.000528 \times 10^{-2} t \text{ Btu/lb-}^\circ\text{F}, \quad (\text{IVA9-1})$$

where  $t$  is in  $^\circ\text{F}$ . This equation then converts to give

$$C_p^\circ = 6.3147 + 1.696464 \times 10^{-3} T \text{ cal degK}^{-1} \text{ gfw}^{-1}. \quad (\text{IVA9-2})$$

The low-temperature data of Burk et al<sup>4</sup> were next joined smoothly with the Armour data to 500°K. This led to  $C_{p,298.15}^\circ = 6.390 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 10.710 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  and  $H_{298.15}^\circ - H_0^\circ = 1.435 \text{ kcal gfw}^{-1}$ . Data between 298.15° and 500°K were numerically integrated on a computer program to give thermodynamic functions. Above 500°K, the Armour equation already cited was used and extrapolated to the melting point. Transition and melting-point data were evaluated as in the earlier report<sup>1</sup> by estimating  $\Delta H_{\text{transition}, 2033^\circ\text{K}}^\circ = 1.650 \pm 0.200 \text{ kcal gfw}^{-1}$ . Also, the heat of fusion was estimated as  $\Delta H_{\text{fusion}, 2495^\circ}^\circ = 5.239 \pm 1.000 \text{ kcal gfw}^{-1}$ . Above the melting point, the heat capacity was estimated as  $8.000 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ , as before.

Recent vapor-pressure measurements for hafnium have been made by Panish and Reif<sup>5</sup> and Lyon.<sup>6</sup> A recalculation of their reported vapor pressures using the presently available free-energy functions gave

Reference	$\Delta H_{f,298.15}^\circ \text{ kcal gfw}^{-1}$
Lyon <sup>6</sup>	146.1515
Panish and Reif <sup>5</sup>	143.6966
Average	144.924

The average value  $\Delta H_{f,298.15}^\circ = 144.924 \text{ kcal gfw}^{-1}$  adopted here is considered to have an uncertainty of about  $\pm 3 \text{ kcal gfw}^{-1}$ . The average is in good agreement with a value of  $142 \pm 6$  derived from vaporization studies of  $\text{HfB}_2$  by Krupka.<sup>7</sup> The latter value is not considered in weighting the above data because it utilizes questionable data for the heat of formation of  $\text{HfB}_2$  and questionable free-energy functions.

From the adopted heat of formation, a boiling point of 4985.40°K was calculated. This is considerably lower than the boiling point of 5536.37 calculated earlier using the estimation that the heat of vaporization of hafnium was 168 kcal gfw<sup>-1</sup>.

### Supplement

After this work was finished, Krikorian<sup>8</sup> referred to some unpublished work by R. G. Bedford. The latter had found that the heat of sublimation of hafnium is  $\Delta H_{298.15} = 148.0$  kcal gfw<sup>-1</sup> in general agreement with the present tabulation. Trulson and Goldstein<sup>9</sup> found a heat of sublimation of  $\Delta H_{298.15} = 149.5 \pm 3.2$  kcal/mole. Heat-capacity data from 298.15° to 1346°K have been reported by Hawkins et al.<sup>10</sup>

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## 10. Iridium

### a. Crystal Structure and Melting Point

Elemental iridium has a face-centered cubic (Al) type of structure.<sup>1</sup> No other allotropic modifications are known.

The melting point was found to be  $2716^{\circ} \pm 3^{\circ}\text{K}$  (corrected to the Temperature Scale of 1948) by Henning and Wensel,<sup>2</sup> and Morris and Scholes.<sup>3</sup> Baird<sup>4</sup> more recently reported the melting point to be  $2683^{\circ} \pm 10^{\circ}\text{K}$ . An average of these temperatures, or  $2700^{\circ} \pm 20^{\circ}\text{K}$ , was adopted herein.

### b. Thermodynamic Properties

#### 1) Heat of fusion

In the absence of experimental data, the entropy of fusion of iridium was estimated to be 2.3 e.u. which corresponded to a heat of fusion of 6.210 Kcal/gfw at  $2700^{\circ}\text{K}$ . An uncertainty of  $\pm 1$  Kcal/gfw was assigned to this quantity.

#### 2) Entropy and heat content at $298.15^{\circ}\text{K}$

The low-temperature heat capacity of iridium was measured by Wolcott,<sup>5</sup> and Clusius and Losa.<sup>6</sup> From these data,  $S_{298}^{\circ}$  and  $H_{298}^{\circ} - H_0^{\circ}$  were calculated to be  $8.497 \pm 0.040$  e.u. and 1.274 Kcal/gfw, respectively. The heat capacity at  $298.15^{\circ}\text{K}$  was taken to be  $6.110 \pm 0.070$  cal/ $^{\circ}\text{K}$ gfw.

#### 3) High-temperature heat content

The high-temperature heat content of iridium was measured by Jaeger and Rosenbohm,<sup>7</sup> and Wöhler and Jochum.<sup>8</sup> Metal purity was not specified in either paper. The data of Jaeger and Rosenbohm,<sup>7</sup> after correction for a revised atomic weight of iridium, may be represented in cal/ $^{\circ}\text{K}$ gfw over the temperature range from  $273^{\circ}$  to  $1877^{\circ}\text{K}$  by equation (IVA10-1),

$$C_p^{\circ} = 5.517 + 1.422 \times 10^{-3}T \quad , \quad (\text{IVA10-1})$$

from which  $C_p^{\circ}$  at  $298.15^{\circ}\text{K}$  is 5.941 cal/ $^{\circ}\text{K}$ gfw. The data of Wöhler and Jochum<sup>8</sup> were tabulated as average specific heats. These data were recalculated to give the "true" heat capacities

in cal/°K gfw and may be represented in the temperature range from 298° to 1273°K by equation (IVA10-2)

$$C_p^\circ = 5.292 + 2.652 \times 10^{-3}T \quad (\text{IVA10-2})$$

From this equation, the heat capacity at 298.15°K was found to be 6.083 cal/°K gfw.

The agreement between these two sets of data was not good because the heat-capacity equations have significantly different temperature coefficients. Kelley<sup>9</sup> adopted the results of Jaeger and Rosenbohm,<sup>7</sup> but he added a small amount to the constant term of the heat-capacity equation. However, near 298.15°K, the heat capacities of Jaeger and Rosenbohm<sup>7</sup> increased more slowly with temperature than would be expected from the low-temperature data of Clusius and Losa.<sup>6</sup> The heat capacities of Wöhler and Jochum,<sup>8</sup> on the other hand, joined well with the low-temperature data, but they appeared to extrapolate to unreasonably large values at high temperatures. Therefore, equation (IVA10-3) was adopted to represent the heat capacity of iridium in cal/°K gfw from 298.15°K to the melting point.

$$C_p^\circ = 5.997 + 1.422 \times 10^{-3}T - \frac{0.2763 \times 10^5}{T^2} \quad (\text{IVA10-3})$$

This equation gave heat capacities which joined smoothly with the low-temperature data and were close to the values of Wöhler and Jochum<sup>8</sup> up to about 500°K. Above that temperature, heat-capacity differences between values from the adopted equation and those of Jaeger and Rosenbohm<sup>7</sup> approached a constant value of 0.48 cal/°K gfw. The assigned uncertainties were based on the spread of the two sets of high-temperature data.

In the absence of experimental data, the heat capacity of liquid iridium was assumed to be 10.000 cal/°K gfw.

#### 4) Standard heat of formation of the monatomic gas

The vapor pressure of iridium was measured by Panish and Reif,<sup>10</sup> Hampson and Walker,<sup>11</sup> and Dreger and Margrave.<sup>12</sup> The data of Dreger and Margrave<sup>12</sup> were apparently subject to a further correction,<sup>11</sup> and therefore, were not considered further. With the thermodynamic functions tabulated here for iridium, the "Third-Law" method was used to calculate a heat of formation for the

monatomic gas at 298.15°K of  $157.960 \pm 0.800$  Kcal/gfw from the data of Panish and Reif,<sup>10</sup> and of  $159.610 \pm 0.900$  Kcal/gfw from the data of Hampson and Walker,<sup>11</sup>. In adopting a value of  $158.000 \pm 1.000$  Kcal/gfw for this compilation, more weight was given to the data of Panish and Reif<sup>10</sup> because their temperature measurements did not require an emissivity correction.

#### 5) Boiling point and heat of vaporization

An extrapolation of  $\Delta F_i^\circ$  of the ideal gas to zero gave the normal boiling point of iridium as  $4711.55^\circ \pm 235^\circ\text{K}$ . The heat of vaporization at the normal boiling point was calculated to be  $141.960 \pm 8.940$  Kcal/gfw. Accordingly,  $\Delta S_v^\circ$  was found to be  $30.130 \pm 4.475$  e.u. Stull and Sinke<sup>13</sup> estimated the normal boiling point as  $4400^\circ\text{K}$ , which gave a heat of sublimation at 298.15°K of 150 Kcal/gfw and a heat of vaporization at  $4400^\circ\text{K}$  of 134.700 Kcal/gfw.

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## 11. Lanthanum

An analysis of thermochemical data for lanthanum was not initiated during this project; however, a bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.

## 12. Magnesium

Magnesium vapor-pressure measurements recently reported by Schmahl and Sieben<sup>1</sup> had not been included in the previous discussion of the thermodynamic functions of that element in the summary technical report<sup>2</sup> on contract AF33(616)-7327. The new data were reported in the form of vapor-pressure equations. Third-Law treatment of the new data yielded a value of  $\Delta H_{f298}^{\circ} = 35.00$  kcal/gfw. This value was below the average of  $35.340 \pm 0.250$  kcal/gfw previously adopted and appears to be too low in view of the large number of determinations which fell within the assigned uncertainty limits. It is, therefore, recommended to retain the value of  $\Delta H_{f298}^{\circ}$  previously adopted.

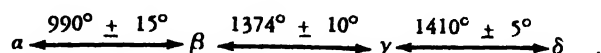
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### 13. Manganese

#### a. Crystal Structure, Transition Points, and Melting Point

Elemental manganese had been reported to have four crystalline modifications for which the following transformation temperatures in °K were selected:



Sully<sup>1</sup> summarized most of the experimental data concerning transformation temperatures for manganese. Additional data were obtained by Dean and others,<sup>2</sup> and Armstrong and Grayson-Smith.<sup>3</sup> The adopted  $\beta$ - $\gamma$  and  $\gamma$ - $\delta$  transformation temperatures were taken from the manganese heat-content measurements of Naylor.<sup>4, 5</sup> The temperature given by Naylor for the sluggish  $\alpha$ - $\beta$  transformation, 1000°K, was an upper limit. An average of his  $\alpha$ - $\beta$  transformation temperatures on heating and cooling through the transition was 980°K. The heat-capacity measurements of Armstrong and Grayson-Smith<sup>3</sup> revealed the  $\alpha$ - $\beta$  transition temperature to be 990°K.

$\alpha$ -Mn was found to have a body-centered cubic structure, type A1;<sup>6-11</sup> the structure of  $\beta$ -Mn was found to be a primitive cubic, A13 type;<sup>7,9-13</sup> the structure of  $\gamma$ -Mn (in the temperature range of thermodynamic stability) was found to be the face-centered cubic, A1 type;<sup>13, 14</sup> and  $\delta$ -Mn was found to have a body-centered cubic, A2-type structure.<sup>13</sup>  $\gamma$ -Mn had been obtained at room temperature as a face-centered tetragonal crystal by electrodeposition of the metal.<sup>4, 15, 16</sup> However, this form could not be retained completely by quenching from a temperature at which it was stable. The tetragonal structure could be stabilized at low temperatures in manganese alloys.<sup>1</sup> The rate of transformation of metastable  $\gamma$ -Mn to  $\alpha$ -Mn at various temperatures was studied by Potter, Lukens, and Huber.<sup>16</sup> At 298°K, the half-time of the  $\gamma$ - $\alpha$  transformation was 238 hours; at 373°K, the half-time was 15 minutes; and at 433°K, it was 7.7 seconds. The transformation temperature between the tetragonal and face-centered cubic structures of  $\gamma$ -Mn as a function of the manganese content of manganese-copper alloys was studied by Basinski and Christian.<sup>17</sup>

Sully<sup>1</sup> reviewed manganese melting point determinations and selected a temperature of  $1517^{\circ} \pm 3^{\circ}$ K for the melting point, which was adopted for the present compilation. The given uncertainty covered six of eight determinations reported since 1927 as listed by Sully.<sup>1</sup> Moser, Raub, and Vincke<sup>18</sup> reported a melting point of 1520°K.



b. Thermodynamic Properties

1) Heats of transition and fusion

The heats of transition adopted were those calculated from the analytical representations of the high-temperature heat-content measurements of Naylor<sup>4, 5</sup> at the following adopted transition temperatures:

TABLE 14  
ADOPTED TRANSITION TEMPERATURES OF Mn

Transition	Temperature	Heat of Transition
	°K	cal/gfw
$\alpha-\beta$	990	$531 \pm 80$
$\beta-\gamma$	1374	$549 \pm 80$
$\gamma-\delta$	1410	$436 \pm 60$

Other relatively reliable values for the heat of the  $\alpha-\beta$  transformation were 615 cal/gfw at 1012°K reported by Southard and Shomate,<sup>19</sup> and 450 cal/gfw reported by Armstrong and Grayson-Smith.<sup>3</sup> There were no other reliable measurements of the heats of the  $\beta-\gamma$  and  $\gamma-\delta$  transformations.

The heat of fusion of manganese given by Kelley, Naylor, and Shomate,<sup>5</sup> 3500 cal/gfw, was adopted herein. This value was based on a heat of fusion of 3450 cal/gfw at 1493°K reported by Umino.<sup>20</sup> Kelley<sup>21</sup> obtained a value of 3650 cal/gfw from analysis of phase data for several manganese alloys. Kubaschewski<sup>22</sup> selected a lower heat of fusion equal to  $3200 \pm 600$  cal/gfw from the same sources on the assumption that the thermal effects involved included a contribution from the then unknown  $\gamma-\delta$  transformation. The problem of finding a suitable container material for liquid manganese apparently complicated the experimental measurement of the heat of fusion.

2) Low-temperature heat capacity

a)  $\alpha$ -Mn

The low-temperature heat capacity of  $\alpha$ -Mn has been measured by Gaumer,<sup>23</sup> Wolcott,<sup>24</sup> Guthrie, Friedberg, and Goldman,<sup>25</sup> Booth, Hoare, and Murphy,<sup>26</sup> Elson, Grayson-Smith, and Wilhelm,<sup>27</sup> Armstrong and Grayson-Smith,<sup>28</sup> Kelley,<sup>29</sup> and

Shomate.<sup>30</sup> There has been considerable interest in the heat capacity of manganese at very low temperatures since the metal has one of the highest electronic specific heats known.

Kelley and King<sup>31</sup> reported  $S_{298}^{\circ}$  for  $\alpha$ -Mn to be  $7.640 \pm 0.040$  e. u. from the measurements of Booth, Hoare, and Murphy<sup>26</sup> and Shomate.<sup>30</sup> This value was adopted herein. The results of Wolcott,<sup>24</sup> Elson, Grayson-Smith, and Wilhelm,<sup>27</sup> and Armstrong and Grayson-Smith<sup>28</sup> agreed well with each other but were some 25 percent higher than those of Guthrie, Friedberg, and Goldman,<sup>25</sup> and Booth, Hoare, and Murphy.<sup>26</sup>  $S_{298}^{\circ}$  for  $\alpha$ -Mn was calculated by Stull and Sinke<sup>32</sup> and by Hultgren and others,<sup>33</sup> to be 7.650 e. u.

b)  $\beta$ -Mn

The low-temperature heat capacity of metastable  $\beta$ -Mn (produced by quenching  $\beta$ -Mn at 1393°K in water) was measured by Booth, Hoare, and Murphy.<sup>26</sup>

c)  $\gamma$ -Mn

Shomate<sup>5, 30</sup> measured the low-temperature heat capacity of metastable  $\gamma$ -Mn (produced by electrolytic decomposition) from 53° to 297°K. From these data, Kelley and King<sup>31</sup> calculated an  $S_{298}^{\circ}$  value of  $7.720 \pm 0.040$  e. u. for  $\gamma$ -Mn, of which 0.49 e. u. was from an extrapolation below 53°K.

3) High-temperature heat content

The high-temperature heat content or heat capacity of manganese was measured by Armstrong and Grayson-Smith,<sup>3</sup> Laemmel,<sup>34</sup> Naylor,<sup>4, 5</sup> Southard and Shomate,<sup>19</sup> Stücker,<sup>35</sup> Umino,<sup>20</sup> and Wüst, Meuthen, and Durrer.<sup>36</sup>

The data of Naylor were adopted, with the exception of the noted modification of the  $\alpha$ - $\beta$  transition temperature, and extrapolated to the melting point. The following heat-capacity equations (in cal/°K gfw) were used over the temperature range of 298° to 1517°K together with the heats of transition given above:

$$C_p^{\circ} (\alpha\text{-Mn}) = 5.704 + 3.380 \times 10^{-3} T - 0.375 \times 10^5 T^{-2} \quad (\text{IVA13-1})$$

$$C_p^{\circ} (\beta\text{-Mn}) = 8.330 + 0.660 \times 10^{-3} T \quad (\text{IVA13-2})$$

$$C_p^\circ (\gamma\text{-Mn}) = 10.700 \quad (\text{IVA13-3})$$

$$C_p^\circ (\delta\text{-Mn}) = 11.300 \quad (\text{IVA13-4})$$

The agreement between the results of the various authors was not good. Other measurements on  $\alpha\text{-Mn}$  with metal of known high purity by Armstrong and Grayson-Smith,<sup>3</sup> and Southard and Shomate<sup>19</sup> gave heat capacities 1 to 3 percent lower than the adopted data. However, Naylor's data were preferred as they joined well with the low-temperature heat-capacity measurements and formed part of an internally consistent set of data for all crystalline modifications.

Armstrong and Grayson-Smith measured the heat capacity of  $\beta\text{-Mn}$  over a narrow range of temperatures less than 100° above the  $\alpha\text{-}\beta$  transition temperature. Their data showed a greater temperature dependence of the heat capacity of  $\beta\text{-Mn}$  than that found by Naylor although the two sources were in excellent agreement at 1073°K. Southard and Shomate's results for  $\beta\text{-Mn}$  were only in fair agreement with those of Naylor. Naylor's results were the only reliable ones for  $\gamma\text{-}$  and  $\delta\text{-Mn}$ . He also derived a heat-capacity equation for  $\gamma\text{-Mn}$  in the temperature range of 298° to 1374°K, where the latter modification was metastable. Recalculation of this equation with the thermodynamic functions for  $\alpha\text{-Mn}$  from this compilation yielded equation (IVA13-5) for  $C_p^\circ$  in cal/°K gfw over the temperature range of 298° to 1374°K.

$$C_p^\circ (\gamma\text{-Mn}) = 5.997 + 3.625 \times 10^{-3}T - 0.434 \times 10^{-5}T^2 \quad (\text{IVA13-5})$$

An extrapolation of this equation to the range of stability of  $\gamma\text{-Mn}$  gave an average heat capacity of 11.020 cal/°K gfw as compared with the experimental value of 10.700 cal/°K gfw. Thermodynamic functions of metastable  $\gamma\text{-Mn}$  had been given elsewhere;<sup>5, 33, 37</sup> however, they were not included in the present compilation which superseded them.

#### 4) Standard heat of formation of the gas at 298.15°K

The vapor pressure of manganese was measured by Bauer and Brunner,<sup>38</sup> McCabe and Hudson,<sup>39</sup> Butler, McCabe, and Paxton,<sup>40</sup> Evseev and Pozharskaya,<sup>41</sup> and Woolf, Zellars, Foerster, and Morris.<sup>42</sup>

The following heats of formation of the gas in kcal/gfw at 298.15°K were calculated with the Third-Law method and vapor-pressure data from the latter sources and thermodynamic functions for manganese from the present compilation:

Source	$\Delta H_{f298}^{\circ}$ of the Gas
Bauer and Brunner <sup>38</sup>	68.150 $\pm$ 0.650
McCabe and Hudson <sup>39</sup>	67.110 $\pm$ 0.400
Butler, McCabe, and Paxton <sup>40</sup>	67.210 $\pm$ 0.250
Woolf <u>et al</u> <sup>42</sup>	66.780 $\pm$ 0.100

From the last three values, a standard heat of formation of 67.000  $\pm$  0.300 kcal/gfw was selected for Mn as an ideal gas at 298.15°K.

Only a Second-Law treatment was possible for the data of Evseev and Pozharskaya.<sup>41</sup> At 298.15°K, a heat of formation of 68.760 kcal/gfw was calculated for the gas with their vapor-pressure equation. However, by neglecting deviating data at one temperature, one can make a new plot giving a heat of formation near the adopted value.

Stull and Sinke<sup>32</sup> reported, from a private communication from Brewer, the heat of formation of the gas to be 66.730 kcal/gfw at 298.15°K.

The normal boiling point and corresponding heat of vaporization were calculated to be 2318.80°  $\pm$  50°K and 52.753  $\pm$  2.280 kcal/gfw, respectively.

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#### 14. Molybdenum

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.

#### 15. Neodymium

An analysis of thermochemical data for neodymium was not initiated during this project; however, a bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.

## 16. Niobium

### a. Crystal Structure and Melting Point

Elemental niobium is of particular interest in modern-day technology over a tremendous range of temperatures. Interest in its superconductivity leads to very-low-temperature studies while high-temperature applications are on the other end of the temperature scale. Recent comprehensive works with data on niobium include the books of Miller<sup>1</sup> and Douglass and Kunz.<sup>2</sup>

From the work of Hansen and Anderko,<sup>3</sup> the normal crystalline form of niobium has a body-centered-cubic (bcc) structure of the A2 type with lattice parameter 3.3007 Å. Except for a change from the superconducting to the normal lattice near 9.09°K reported by Boorse, Hirshfeld, and Leupold,<sup>4</sup> it is believed that niobium retains its bcc structure to the melting point.

Various melting points have been reported, and several of the earlier ones were reviewed by Stull and Sinke;<sup>5</sup> they are all tabulated below.

MELTING POINTS OF NIOBIUM

Reference	T(°K)
Samsonov <sup>6</sup>	2773
Reimann and Grant <sup>7</sup>	2770
Glassner <sup>8</sup>	2760
Schofield <sup>9</sup>	2741
Goldsmith <u>et al</u> <sup>10</sup>	2740
Buehler <sup>11</sup>	2733
Wilhelm <u>et al</u> <sup>12</sup>	2693
Elliott and Komjathy <sup>13</sup>	2688

From these values, the intermediate value at 2741°K given by Schofield<sup>9</sup> was accepted.



## b. Thermodynamic Properties

### 1) Heat of fusion

Experimental determinations of the heat of fusion of niobium were not available; however, there were several estimated values. Stull and Sinke<sup>5</sup> give 6400 cal gfw<sup>-1</sup>, Glassner<sup>8</sup> 5800 cal gfw<sup>-1</sup>, and Elliott and Gleiser<sup>14</sup> 6430 cal gfw<sup>-1</sup>. For the present calculations, the Stull and Sinke value of 6400 cal gfw<sup>-1</sup> was used; the probable accuracy of this value is believed to be  $\pm 1000$  cal gfw<sup>-1</sup>.

### 2) Entropy and heat content at 298.15°K

Heat-capacity data at very low temperatures in the superconductivity region have been performed by Boorse *et al.*<sup>4</sup> Other investigations, also at very low temperatures, include those of Brown, Zemansky, and Boorse<sup>15-17</sup> for the ranges 2° to 11°K, and 65° to 75°K, and of Chou, White, and Johnston<sup>18</sup> from 1° to 30°K. Kelley<sup>19</sup> has analyzed the data of the last four references. Using an extrapolation from 75° to 298.15°K, he obtained  $S_{298.15}^{\circ} = 9.0 \pm 0.4$  cal °K<sup>-1</sup> gfw<sup>-1</sup>. This value was accepted in the present tabulations. The value of  $H_{298}^{\circ} - H_0^{\circ}$  was not listed by Kelley, and the value of 1264 cal gfw<sup>-1</sup> given by Stull and Sinke<sup>5</sup> was used. This value is also based on an extrapolation procedure over the same temperature range used by Kelley and had led to an entropy estimate of 8.73 cal °K<sup>-1</sup> gfw<sup>-1</sup>. Considering the range of this extrapolation, the agreement between the Kelley and Stull and Sinke data is good. The entropy value chosen is 0.3 cal °K<sup>-1</sup> gfw<sup>-1</sup> larger than the value of  $8.70 \pm 0.1$  cal °K<sup>-1</sup> gfw<sup>-1</sup> chosen by Hultgren *et al.*,<sup>20</sup> who utilized the data 11° to 273°K by Clusius, Franzosini, and Piesbergen.<sup>21</sup> The last authors had found  $S_{298.15}^{\circ} = 8.58$  cal °K<sup>-1</sup> gfw<sup>-1</sup>. In future revision of this table, it may be desirable to use this lower entropy data although the change is relatively minor.

### 3) High-temperature heat content

Kelley<sup>22</sup> gives a linear equation for the high-temperature heat capacity of the form  $C_p^{\circ} = 5.66 + 0.96 \times 10^{-3} T$  cal °K<sup>-1</sup> gfw<sup>-1</sup> which he extrapolates to the melting point. This equation was based on the work of Jaeger and Veenstra,<sup>23, 24</sup> who reported data from 273° to 1828°K. The Kelley equation was adopted in the present work as it gives good agreement with the recent work of Gel'd and Kusenko,<sup>25</sup> who reported  $C_p^{\circ} = 5.41 + 1.24 \times 10^{-3} T$  for the range  $298.15 \leq T \leq 1740^{\circ}\text{K}$ . At 1000°K, the two sets of data deviate by only 0.45 percent; while, at 2000°K, the Gel'd and Kusenko data are about 4 percent higher.

A determination of high-temperature heat-capacity data by Fieldhouse, Hedge, and Lang<sup>26</sup> for the range 533° to 1811°K gives good agreement at lower temperatures but is higher than the Kelley or Gel'd and Kusenko data at the highest temperature; i. e., 1800°K.

Above the melting point, the heat capacity of liquid Nb was estimated to be  $8.00 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$  following Kelley.<sup>22</sup>

#### 4) Standard heat of formation of the gas at 298.15°K

Stull and Sinke<sup>5</sup> had derived a value of  $177.5 \text{ kcal gfw}^{-1}$  for the heat of sublimation of niobium at 298.15°K, based on the work of Reimann and Grant.<sup>7</sup> A more recent work by Speiser *et al*<sup>27</sup> gave a value of  $172.53 \text{ kcal gfw}^{-1}$ . For the present tabulation, the vapor-pressure data of Speiser *et al*<sup>27</sup> were recalculated, using free-energy functions for solid and gaseous niobium from the present calculations to give  $\Delta H_{\text{sub}, 298.15}^\circ = 171.836 \text{ kcal gfw}^{-1}$ . The normal boiling point was calculated to be 5031.58°K, and the associated heat of vaporization was found to be  $162.573 \text{ kcal gfw}^{-1}$ . The calculated boiling point agrees well with a value of 5007°K found by Hultgren *et al*,<sup>20</sup> and fairly well with the earlier Stull and Sinke<sup>5</sup> value of 5200°K. It should be pointed out that the calculated boiling point is subject to an uncertainty of approximately 200°K.

#### 5) Ideal monatomic gas

The thermodynamic functions for niobium ideal monatomic gas were from an earlier publication,<sup>28</sup> based on the energy levels of Moore.<sup>29</sup>

### Supplement

Blackburn<sup>30</sup> has reported new vapor-pressure data for Nb. He found that  $\Delta H_{f0}^\circ = 174.8 \text{ kcal gfw}^{-1}$ . This value is seen to be in moderate agreement with the value previously accepted here. Lowenthal<sup>31</sup> made heat-capacity measurements in the range 1471° to 2260°K.

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## 17. Nitrogen

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. 1, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.

## 18. Osmium

### a. Crystal Structure and Melting Point

Elemental osmium had been reported to have a hexagonal close-packed (A3) type of structure.<sup>1, 2, 3, 4</sup> There appeared to be no evidence for solid-state transitions.

The melting point of osmium was recently experimentally measured by three groups of workers. Values of 3273°K,<sup>5</sup> 3283° ± 10°K,<sup>6</sup> and 3318° ± 30°K<sup>7</sup> were reported. A value of 3290° ± 30°K was adopted for this compilation. The melting point had been previously estimated as 3000°K.<sup>8</sup>

### b. Thermodynamic Properties

#### 1) Heat of fusion

The heat of fusion of osmium had not been experimentally measured. An entropy of fusion of 2.3 e.u. was assumed which corresponded to a heat of fusion of 7.567 Kcal/gfw at 3290°K. An uncertainty of ± 1.200 Kcal/gfw was assigned to the heat of fusion.

#### 2) Entropy and heat content at 298.15°K

In the absence of recent experimental data, Kelley and King<sup>9</sup> adopted a value for  $S_{298}^0$  of  $7.8 \pm 0.5$  e.u. from Lewis and Gibson's<sup>10</sup> computations with some early measurements of Dewar.<sup>11</sup> The same value was adopted for this compilation.  $H_{298}^0 - H_0^0$  was estimated herein to be 1210 cal/gfw.

### 3) High-temperature heat content

The only experimental measurement of the high-temperature heat content and heat capacity of osmium appeared to be that of Jaeger and Rosenbohm.<sup>12</sup> Kelley's<sup>13</sup> equation for their data in cal/°K gfw

$$C_p^\circ = 5.690 + 0.880 \times 10^{-3}T \quad (\text{IVA18-1})$$

was adopted for this compilation and extrapolated to the melting point.

In the absence of experimental data, the heat capacity of liquid osmium was assumed to be  $9.000 \pm 0.450$  cal/°K gfw.

### 4) Heat of formation of the monatomic gas

The vapor pressure of osmium had been measured by Panish and Reif.<sup>14</sup> From their vapor pressure data and thermodynamic functions for osmium tabulated in this compilation, the standard heat of formation of the gas at 298.15°K was calculated to be  $187.400 \pm 1.500$  Kcal/gfw. This value was considerably larger than the estimate of 160.000 Kcal/gfw made earlier by Stull and Sinke.<sup>15</sup>

The normal boiling point of osmium was calculated to be  $5269.57^\circ \pm 310^\circ\text{K}$ , which was much higher than the  $4500^\circ\text{K}$  listed by Stull and Sinke.<sup>15</sup> The heat of vaporization at the normal boiling point was found to be  $176.401 \pm 9.820$  Kcal/gfw. The entropy of vaporization was, therefore,  $33.476 \pm 1.863$  e.u. at the boiling point.

### 5) Thermodynamic functions

The thermodynamic functions of the ideal monatomic gas of osmium reported herein are a revision of the previous tabulation in the first summary technical report.<sup>16</sup> The new tabulation is based on the energy level scheme recently published by van Kleef<sup>17</sup> and van Kleef and Klinkenberg.<sup>18</sup>

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## 19. Oxygen

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for this element can be found in sections VIII and IX, volume 2 of this work.



## 20. Platinum

### a. Crystal Structure and Melting Point

Elemental platinum was found to have a face-centered cubic, Al-type structure.<sup>1-3</sup> No other allotropic modifications were reported.

A melting point of  $2043^{\circ} \pm 3^{\circ}\text{K}$  was taken from the results of Roeser, Caldwell, and Wensel,<sup>4</sup> Hoffmann and Tingwaldt,<sup>5</sup> and Schofield<sup>6</sup> after correction to the International Temperature Scale of 1948. A melting point of  $2033^{\circ} \pm 2^{\circ}\text{K}$  was also reported later;<sup>7</sup> however, it was not considered as reliable as the earlier value.

### b. Thermodynamic Properties

#### 1) Heat of fusion

In the absence of experimental data, an entropy of fusion of  $2.300 \pm 0.390$  e. u. was assumed. This corresponded to a heat of fusion of 4.699 kcal/gfw, to which an uncertainty of  $\pm 0.800$  kcal/gfw was assigned.

#### 2) Entropy and heat content at $298.15^{\circ}\text{K}$

The low-temperature heat capacity of platinum was measured by Rayne,<sup>8</sup> Ramanathan and Srinivasan,<sup>9</sup> Budworth, Hoare, and Preston,<sup>10</sup> Kok and Keesom,<sup>11</sup> Simon and Zeidler,<sup>12</sup> and Clusius, Losa, and Franzosini.<sup>13</sup> From the data of the last three sources, Kelley and King<sup>14</sup> calculated  $S_{298}$  to be  $9.950 \pm 0.050$  e. u. The same value was given in the compilation of Clusius, Losa, and Franzosini<sup>13</sup> (calculated from their results by Hultgren and others<sup>15</sup>) and was adopted herein.  $H_{298} - H_0$  was taken to be 1.372 kcal/gfw from Hultgren and others.<sup>15</sup>

#### 3) High-temperature heat content

The platinum tables in the present compilation were based on the high-temperature heat-content measurements of Jaeger and Rosenbohm,<sup>16</sup> Jaeger, Rosenbohm, and Bottema,<sup>17</sup> and White.<sup>18</sup> Kelley's<sup>19</sup> article may be consulted for references to a number of other measurements.

The heat-capacity results of Jaeger and Rosenbohm<sup>16</sup> were represented (in cal/ $^{\circ}\text{K}$  gfw) from  $273^{\circ}$  to  $473^{\circ}\text{K}$  and  $473^{\circ}$  to  $1873^{\circ}\text{K}$ , respectively, by the equations

$$C_p^\circ = 5.567 + 2.273 \times 10^{-3} T - 0.0942 \times 10^{-5} T^2, \quad (\text{IVA20-1})$$

and

$$C_p^\circ = 5.831 + 1.238 \times 10^{-3} T. \quad (\text{IVA20-2})$$

The results of Jaeger, Rosenbohm, and Bottema<sup>17</sup> were represented in the same units over the temperature range from 273° to 1673°K by the equation

$$C_p^\circ = 5.846 + 1.248 \times 10^{-3} T - 3.170 \times 10^{-8} T^2, \quad (\text{IVA20-3})$$

and those of White<sup>18</sup> were likewise represented by the equation

$$C_p^\circ = 5.841 + 1.249 \times 10^{-3} T. \quad (\text{IVA20-4})$$

For the present compilation, the following equations were adopted to join smoothly the low-temperature (298° to 500°K) and high-temperature (500° to 2043°K) data, respectively, in cal/°K gfw:

$$C_p^\circ = 6.028 + 0.969 \times 10^{-3} T - \frac{0.1220 \times 10^5}{T^2}, \quad (\text{IVA20-5})$$

and

$$C_p^\circ = 5.810 + 1.260 \times 10^{-3} T - \frac{0.060 \times 10^5}{T^2}. \quad (\text{IVA20-6})$$

The heat capacity of liquid platinum had not been measured and was assumed to be 8.500 cal/°K gfw to be consistent with the above equations. Kelley<sup>19</sup> assumed it to be 8.300 cal/°K gfw.

#### 4) Standard heat of formation of the gas at 298.15°K

The vapor pressure of platinum was measured by Jones, Langmuir, and Mackay,<sup>20</sup> Dreger and Margrave,<sup>21</sup> and Hampson and Walker.<sup>22</sup> The data of Jones, Langmuir, and Mackay<sup>20</sup> were corrected to the International Temperature Scale of 1948. The following values for the heat of formation of the gas at 298.15°K were calculated with the Third-Law method and the thermodynamic functions for platinum given herein:

Source of Vapor-Pressure Data	$\Delta H_{f298}^{\circ}$
	kcal/gfw
Jones, Langmuir, and Mackay <sup>20</sup>	134.890 $\pm$ 1.100
Dreger and Margrave <sup>21</sup>	135.180 $\pm$ 1.200
Hampson and Walker <sup>22</sup>	135.010 $\pm$ 0.900

A value of 135.100  $\pm$  0.300 kcal/gfw was adopted for the present compilation.

The normal boiling point was calculated to be 4108.34°  $\pm$  95°K, and the associated heat of vaporization was found to be 121.519  $\pm$  5.670 kcal/gfw. These quantities were very little changed from those given by Stull and Sinke.<sup>23</sup>

The ideal monatomic gas properties were taken from the previous calculation on this project.<sup>24</sup>

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## 21. Rhenium

### a. Crystal Structure and Melting Point

Elemental rhenium was found to have a hexagonal close-packed, A3-type structure.<sup>1-7</sup> No other allotropic modifications were reported.

The melting point of  $3453^{\circ} \pm 20^{\circ}\text{K}$  reported by Sims, Craighead, and Jaffee<sup>1</sup> was adopted as the best value. Previous measurements had established values of  $3440^{\circ} \pm 60^{\circ}\text{K}$ <sup>5</sup> and  $3433^{\circ}\text{K}$ .<sup>8</sup>

### b. Thermodynamic Properties

#### 1) Heat of fusion

The heat of fusion of rhenium had not been measured. An entropy of fusion of  $2.300 \pm 0.440$  e.u. was assumed, corresponding to a heat of fusion of 7.942 kcal/gfw. An uncertainty of  $\pm 1.500$  kcal/gfw was assigned to the heat of fusion.

#### 2) Entropy and heat content at 298.15°K

The low-temperature heat capacity of rhenium was measured by Keesom and Bryant,<sup>9</sup> Wolcott,<sup>10</sup> Horowitz and Daunt,<sup>11</sup> and Smith, Oliver, and Cobble.<sup>12</sup> Rhenium was found to have a superconducting transition at about 2°K.<sup>13-15</sup>

The adopted values for  $S_{298}^{\circ}$  and  $H_{298}^{\circ} - H_0^{\circ}$  were based on the measurements of Smith, Oliver, and Cobble<sup>12</sup> as was the value for  $S_{298}$  tabulated by Kelley and King.<sup>16</sup> The  $C_p^{\circ}$  value of  $6.160 \pm 0.04$  cal/°K gfw at 298.15°K adopted herein represented a slight upward revision of the smoothed  $C_p^{\circ}$  at that temperature given in the original reference.  $S_{298}$  was calculated to be  $8.886 \pm 0.050$  e.u. and  $H_{298} - H_0$  was calculated to be 1.307 kcal/gfw.

#### 3) High-temperature heat content

The high-temperature heat content of rhenium was measured by Jaeger and Rosenbohm.<sup>8</sup> Their data in cal/°K gfw were represented between 273° and 1474°K by the equation

$$C_p^{\circ} = 5.726 + 1.234 \times 10^{-3} T \quad (\text{IVA21-1})$$

Kelley<sup>17</sup> used a different equation on the basis of the same measurements

$$C_p^\circ = 5.660 + 1.300 \times 10^{-3} T \quad . \quad (\text{IVA21-2})$$

Sims and others<sup>18</sup> reported relative values of the heat capacity from 1620° to 2690°K obtained by a "hot-wire" method. These results had only limited precision. The data suggested, however, that the heat capacity was increasing with temperature more rapidly than a simple linear dependence. They adjusted the low-temperature portion of their data to the high-temperature portion of the results of Jaeger and Rosenbohm<sup>8</sup> and obtained thereby a heat capacity of about 9.5 cal/°K gfw at 2700°K. An extrapolation of Jaeger and Rosenbohm's data<sup>8</sup> would give a heat capacity of 9.06 cal/°K gfw at that temperature, and Kelley's equation<sup>17</sup> would give a value of 9.17 cal/°K gfw.

Jaeger and Rosenbohm's equation<sup>8</sup> gave a heat capacity approximately 0.06 cal/°K gfw lower than the adopted value at 298.15°K. To join the low-temperature data in cal/°K gfw to that of Jaeger and Rosenbohm<sup>8</sup> and also, follow the temperature dependence suggested by Sims and others<sup>18</sup> above 1600°K, the following equation was adopted for temperatures from 298°K to the melting point:

$$C_p^\circ = 5.883 + 0.876 \times 10^{-3} T + 0.0177 \times 10^{-5} T^2 \quad . \quad (\text{IVA21-3})$$

This equation agreed with the equation of Jaeger and Rosenbohm<sup>8</sup> to  $\pm 0.02$  cal/°K gfw between 500° and 1500°K.

In the absence of experimental data, the heat capacity of liquid rhenium was assumed to be 11.000 cal/°K gfw to be consistent with the above equations. An estimate of 10.8 cal/°K gfw was adopted by Stull and Sinke<sup>19</sup> from Sherwood and others.<sup>20</sup>

#### 4) Standard heat of formation of the gas at 298.15°K and the boiling point

The vapor pressure of rhenium was measured by Sherwood and others.<sup>20</sup> The standard heat of formation of the gas at 298.15°K was herein calculated by the Third-Law method to be  $185.370 \pm 1.500$  kcal/gfw from their vapor-pressure data and the thermodynamic functions for rhenium tabulated herein. The normal boiling point and the corresponding heat of vaporization were calculated to be  $5960.67 \pm 260^\circ\text{K}$  and  $168.315 \pm 12.940$  kcal/gfw, respectively. These quantities did not differ greatly from those given by Stull and Sinke.<sup>19</sup>

## 5) Ideal gas properties

The ideal monatomic gas thermodynamic properties of rhenium previously reported<sup>21</sup> were retained.

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## 22. Rhodium

### a. Crystal Structure and Melting Point

Elemental rhodium was found to have a face-centered cubic, Al-type structure at room temperature.<sup>1, 2</sup> An allotropic transformation at approximately 1000°C had been proposed from X-ray, heat-capacity, and thermoelectric measurements.<sup>3-5</sup> However, Bale<sup>6</sup> reported the electrical resistivity and lattice parameter to vary smoothly and continuously from room temperature to 1600°C with metal containing less than 10 ppm metallic impurities. He did observe anomalous behavior toward mechanical working and suggested that either rhodium was uniquely sensitive to impurities or had a mechanism for plastic behavior unlike other face-centered cubic metals. Strong and Bundy,<sup>7</sup> in the course of high-pressure studies on "thermocouple-grade" rhodium, found the electrical resistivity to follow a fairly smooth curve up to the melting point but observed a volume contraction of the metal around 1000° to 1400°C. Rhodium was assumed in the present compilation to be face-centered cubic up to the melting point. However, this fact would need further verification.

The melting point of rhodium was taken to be  $2239^{\circ} \pm 3^{\circ}\text{K}$  from the measurements of Roeser and Wensel,<sup>8</sup> Barber and Schofield,<sup>9</sup> Oriani and Jones,<sup>10</sup> and Haworth and Hume-Rothery.<sup>11</sup>

### b. Thermodynamic Properties

#### 1) Heat of fusion

In the absence of an experimental determination of the heat of fusion of rhodium, an entropy of fusion of 2.300 e. u. was assumed. The corresponding heat of fusion was 5.150 kcal/gfw to which an uncertainty of  $\pm 0.800$  kcal/gfw was assigned.

#### 2) Entropy and heat content at 298.15°K

The low-temperature heat capacity of rhodium was measured by Budworth, Hoare, and Preston,<sup>12</sup> Wolcott,<sup>13</sup> and Clusius and Losa.<sup>14</sup>  $S_{298}^{\circ}$  was taken to be  $7.530 \pm 0.050$  e. u. from Kelley and King's<sup>15</sup> evaluation of the data of Clusius and Losa.<sup>14</sup>  $H_{298} - H_0$  was calculated to be 1.174 kcal/gfw from the same data. The heat-capacity value of  $5.940 \pm 0.070$  cal/°K gfw at 298.15°K was obtained from an extrapolation of the low-temperature data.

### 3) High-temperature heat content

The high-temperature heat content of rhodium was measured by Holzmänn,<sup>16</sup> and Jaeger and Rosenbohm.<sup>5</sup> These two sources gave equations leading to heat capacities which differed by about 0.20 cal/°K gfw at 298.15°K and by about 0.15 cal/°K gfw at 1200°K. The equations had somewhat different temperature dependences. According to Holzmänn,<sup>16</sup> the equation in units of cal/°K gfw over the temperature range of 273° to 1173°K was

$$C_p^\circ = 5.707 + 1.883 \times 10^{-3} T \quad . \quad (\text{IVA22-1})$$

According to Jaeger and Rosenbohm,<sup>5</sup> the equation from 273° to 1573°K in the same units was

$$C_p^\circ = 6.015 - 0.869 \times 10^{-3} T + 4.343 \times 10^{-6} T^2 - 1.816 \times 10^{-9} T^3 \quad . \quad (\text{IVA22-2})$$

Both of these equations yielded heat capacities at 298.15°K larger than the adopted value. Jaeger and Rosenbohm's<sup>5</sup> data showed a maximum in the heat capacity, at about 1500°K, which they interpreted to be caused by an allotropic transition. They also gave results for the assumed high-temperature modification in the temperature range from 1665° to 1877°K.

The herein-adopted representation for the heat capacity of rhodium in cal/°K gfw from 298.15°K to the melting point is

$$C_p^\circ = 5.600 + 2.020 \times 10^{-3} T - \frac{0.2334 \times 10^5}{T^2} \quad (\text{IVA22-3})$$

This equation yields heat capacities which join smoothly with the low-temperature data and agree with the average of the results of Holzmänn,<sup>16</sup> and Jaeger and Rosenbohm<sup>5</sup> between 500° and 1200°K. Above 400°K, it yields values that are 0.05 cal/°K gfw greater at a maximum than those from an equation selected by Kelley<sup>17</sup> to represent the same high-temperature data.

The heat capacity of liquid rhodium was assumed to be 10.000 cal/°K gfw.

### 4) Standard heat of formation of the gas at 298.15°K

The vapor pressure of rhodium was measured by Panish and Reif,<sup>18</sup> Hampson and Walker,<sup>19</sup> and Dreger and Margrave.<sup>20</sup>

A recalculation was made of  $\Delta H_{f298}^{\circ}$  with these vapor-pressure data by the Third-Law method using the thermodynamic functions for rhodium tabulated herein. From the data of Panish and Reif,<sup>18</sup> the standard heat of formation at 298.15°K was calculated to be  $132.900 \pm 0.600$  kcal/gfw. The data of Hampson and Walker<sup>19</sup> gave a value of  $132.640 \pm 1.500$  kcal/gfw, and the data of Dreger and Margrave<sup>20</sup> gave a value of  $134.400 \pm 2.100$  kcal/gfw. The value of 132.770 kcal/gfw was adopted as the best value from the first two sources, and an uncertainty of  $\pm 1.600$  kcal/gfw was assigned to it. The normal boiling point was calculated to be  $3995.89^{\circ} \pm 130^{\circ}\text{K}$ , and the heat of vaporization at the boiling point was found to be  $118.145 \pm 6.570$  kcal/gfw. All of these quantities were very close to earlier estimates of Stull and Sinke.<sup>21</sup>

#### 5) Ideal gas

The thermodynamic properties of the ideal monatomic gas previously reported<sup>22</sup> were retained.

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### 23. Samarium

An analysis of thermochemical data for samarium was not initiated during this project; however, a bibliographic search was made, and any references for the element can be found in sections VIII and IX, volume 2 of this work.

### 24. Scandium

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for the element can be found in sections VIII and IX, volume 2 of this work.

## 25. Silicon

### a. Crystal Structure and Melting Point

Silicon exists in a cubic A4 (i.e., diamond-type) structure with lattice parameter<sup>1</sup>  $a = 5.4282 \text{ \AA}$ .

A melting point of  $1690^\circ\text{K}$  was accepted to be compatible with the recent high-temperature heat-capacity data of Kantor et al<sup>2</sup> discussed in detail later. This is in good agreement with a value of  $1685^\circ\text{K}$  found by Olette,<sup>3</sup> and  $1683^\circ\text{K}$  by Hansen et al.<sup>4</sup>

### b. Thermodynamic Properties

#### 1) Entropy and heat content at $298.15^\circ\text{K}$

Low-temperature heat-capacity data have been reported by Anderson,<sup>5</sup> Nernst and Schweser,<sup>6</sup> Pearlman and Keesom,<sup>7</sup> and Magnus.<sup>8</sup> An analysis of these data<sup>5-7</sup> has been made by Kelley<sup>9</sup> to give  $S_{298.15}^\circ = 4.51 \pm 0.05 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ . Stull and Sinke<sup>10</sup> analyzed the data of the above workers<sup>5-8</sup> and gave values in excellent agreement with that of Kelley. They found  $S_{298.15}^\circ = 4.53 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$  and  $H_{298.15}^\circ - H_0^\circ = 769 \text{ cal gfw}^{-1}$ . The recent work of Gul'myayev and Petrov<sup>11</sup> for the range  $80^\circ$  to  $310^\circ\text{K}$  agrees well with the earlier work. Thus, at  $100^\circ\text{K}$ , their data are only 1.5 percent higher than Pearlman and Keesom; while, at  $300^\circ\text{K}$ , their data are approximately 3 percent lower than the Stull and Sinke data. For the present analysis, the Stull and Sinke data have been used.

#### 2) High-temperature heat content

High-temperature heat-capacity data have been reported by Serebrennikov and Gel'd ( $273^\circ$  to  $1556^\circ\text{K}$ ),<sup>12</sup> Magnus ( $290^\circ$  to  $1175^\circ\text{K}$ ),<sup>8</sup> and Olette ( $1467^\circ$  to  $1825^\circ\text{K}$ ).<sup>3</sup> These sources have been analyzed by Kelley<sup>13</sup> to give

$$C_p^\circ = 5.70 + 0.70 \times 10^{-3}T - 1.04 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}, \quad (\text{IVA25-1})$$

for the range  $298^\circ$  to  $1685^\circ\text{K}$ . Additional high-temperature heat-capacity data for silicon have been reported by Kantor et al<sup>2</sup> for the range  $1200^\circ$  to  $1900^\circ\text{K}$ . They give the equations

$$C_p^\circ = 5.724 + 7.296 \times 10^{-4}T \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}, \quad (\text{IVA25-2})$$

for  $1200 \leq T \leq 1690^\circ\text{K}$ , and

$$C_p^\circ = 6.018 + 5.966 \times 10^{-4}T \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}, \quad (\text{IVB25-3})$$

for  $1690 \leq T \leq 1915^\circ\text{K}$ . At the melting point of  $1690^\circ\text{K}$ , they found  $\Delta H_{\text{fusion}}^\circ = 11950 \text{ cal gfw}^{-1}$ .

For the present tabulation, the Kelley equation which joins smoothly with the low-temperature heat-capacity data was used from  $298.15^\circ$  to  $600^\circ\text{K}$ . From  $600^\circ$  to  $1900^\circ\text{K}$ , a curve joining smoothly with the Kelley equation<sup>13</sup> and fitting the Kantor et al<sup>2</sup> data was used. In reproducing the Kantor data, slight, but insignificant, changes were made. Thus, at  $1300^\circ\text{K}$ ,  $C_p^\circ = 6.628$  was used, whereas the Kantor et al data yield  $C_p^\circ = 6.673 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ . The difference is  $0.045 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ , or 0.67 percent. At the melting point, essentially a continuous function for  $C_p^\circ$  has been used. Thus, the Kantor et al equations give values of 6.957 and  $7.026 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$  for the solid and liquid, respectively, at  $1690^\circ\text{K}$ ; whereas the present value is  $C_p^\circ = 6.972 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ .

### 3) Heat of fusion

Heat-of-fusion data include the following experimental values of  $11,100 \text{ cal gfw}^{-1}$  by Koerber and Oelsen,<sup>14</sup>  $12,100 \pm 400 \text{ cal gfw}^{-1}$  by Olette,<sup>3</sup> and  $11,950 \pm 180 \text{ cal gfw}^{-1}$  by Kantor et al.<sup>2</sup> The most recent value of  $11,950 \text{ cal gfw}^{-1}$  has been used in this tabulation. An uncertainty of  $\pm 200 \text{ cal gfw}^{-1}$  has been assigned to this value.

Above  $1900^\circ\text{K}$  where experimental heat-capacity data for liquid silicon are not available, a simple estimate has been made that the heat capacity is constant and equal to the value tabulated at  $1900^\circ\text{K}$ ; namely,  $C_p^\circ, \text{ liquid} = 7.155 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ .

### 4) Heat of formation of the monatomic gas

Thermodynamic functions for the ideal monatomic gas were calculated earlier<sup>15</sup> based on the energy levels of Moore.<sup>16</sup> Vapor-pressure studies have been made by Davis, Anthrop, and Searcy,<sup>17</sup> Honig,<sup>18</sup> Ruff and Kenschak,<sup>19</sup> Bauer and Brunner,<sup>20</sup> Drowart, DeMaria, and Inghram,<sup>21</sup> Searcy,<sup>22</sup> Drowart and DeMaria,<sup>23</sup> Vidale,<sup>24</sup> Grieson and Alcock,<sup>25</sup> Batdorf and Smits,<sup>26</sup> and Tseplyaeva et al.<sup>27</sup>

The works of Ruff and Kenschak and Bauer and Brunner lead to silicon partial pressures approximately a magnitude too high when compared to recent data, and need not be considered further. The recent work of Tseplyaeva et al<sup>27</sup> also leads to too low a heat of sublimation and hence is not considered further. Other vapor studies include those of Drowart and DeMaria<sup>23</sup> from elemental silicon (activity=unity) and  $\text{SiC}$ ,  $\text{SiC} + \text{C}$  systems, and the  $\text{SiC}$  system by Vidale.<sup>24</sup>

Direct vapor-pressure measurements (i.e., over elemental silicon) were performed elsewhere.<sup>17-21,23,25-27</sup> Vapor pressures of silicon gas over SiC + C were also measured by several authors.<sup>17,21-25</sup> However, because of uncertainties in the heat of formation of SiC, it is believed that more accurate data can be obtained from the direct measurements.

The direct-measurement work of Honig<sup>18</sup> and Drowart et al<sup>21,23</sup> was performed on a mass spectrometer. Honig determined only a Second-Law value; i.e.,  $\Delta H_{f1550K}^{\circ} = 105 \pm 12 \text{ kcal gfw}^{-1}$ , calculated herein as a  $\Delta H_{f298}^{\circ} = 106.377 \pm 12 \text{ kcal gfw}^{-1}$ . The data of Drowart and DeMaria<sup>23</sup> gave a Second-Law value of  $\Delta H_{f1570}^{\circ} = 104 \pm 5 \text{ kcal gfw}^{-1}$ , or  $\Delta H_{f298}^{\circ} = 105.412 \pm 5 \text{ kcal gfw}^{-1}$ . From their data at 1900° K via a Second-Law method,  $\Delta H_{f1900}^{\circ} = 92 \pm 5$  or  $\Delta H_{f298,15}^{\circ} = 105.975 \text{ kcal gfw}^{-1}$  is obtained. A Third-Law treatment of their data gives  $\Delta H_{f298}^{\circ} = 106.846 \text{ kcal gfw}^{-1}$ . These data and the results of recalculations for the additional data of Batdorf and Smits,<sup>26</sup> Davis et al,<sup>17</sup> and Grieveson and Alcock<sup>25</sup> are summarized in table 15.

The data of Batdorf and Smits were read from their curve since they did not tabulate data. The Third-Law value for  $\Delta H_{f298}^{\circ}$ , recalculated from the work of Davis et al,<sup>17</sup> agrees well with their own evaluation. In the case of the Grieveson and Alcock<sup>25</sup> work, two types of experiments were performed; i.e., one used a Knudsen cell, and the other a transportation method. Reference to the Drowart and DeMaria<sup>23</sup> data shows that the corrections for Si<sub>2</sub>(g) and Si<sub>2</sub>C(g) are small in these cases. A trial calculation showed that the effect of these gases at the temperature of the Grieveson and Alcock measurements is to add about 0.2 kcal gfw<sup>-1</sup> to the  $\Delta H_{f298,15}^{\circ}$  values. These corrections have been added to their data reported in table 15.

In reviewing the above data, it seems that the Davis et al<sup>17</sup> weight-loss data represent a good choice. The three weight-loss determinations treated by the Third-Law method show good agreement. Furthermore, these data agree well with the mass-spectrometric Third-Law data of Drowart and DeMaria.<sup>23</sup> For the present purposes, the data of Davis et al<sup>17</sup> have been accepted; i.e.,  $\Delta H_{f298,15}^{\circ} \text{Si} = 108.407 \pm 3.0 \text{ kcal gfw}^{-1}$

In the foregoing analysis, only direct vaporization of Si(g) from Si<sub>metal</sub> has been considered. In addition, there have been several investigations of decomposition of SiC according to the reaction:

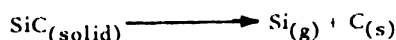




TABLE 15

SUMMARY OF HEATS OF SUBLIMATION OF SILICON--  $\Delta H_{s298.15}$   
(DIRECT MEASUREMENTS)

Reference	Second Law	Third Law	Comments
Batdorf and Smits <sup>26</sup>	106.313	108.895	
Davis <u>et al</u> <sup>17</sup>	---	108.407	
Grieverson and Alcock <sup>25</sup>	109.805	107.699	Knudsen cell; correction of 0.2 kcal gfw <sup>-1</sup> was added to account for Si <sub>2</sub> + Si <sub>2</sub> C
		107.844	Transportation method; correction of 0.2 kcal gfw <sup>-1</sup> was added
Drowart and DeMaria <sup>23</sup>	105.412 ± 5 105.975 ± 5	106.846 ± 3 "	Authors gave 107 ± 3
Honig <sup>18</sup>	106.377 ± 12		

From analysis of several determinations to be discussed in section VB 25.2.1 of this report, a heat of decomposition of SiC of  $\Delta H_{298.15}^{\circ} = 126 \pm 2 \text{ kcal gfw}^{-1}$  is accepted; and for a heat of formation of SiC,  $\Delta H_{\text{SiC}, 298.15}^{\circ} = -16.5 \pm 3 \text{ kcal gfw}^{-1}$ . These data yield  $\Delta H_{\text{sub, elemental Si}, 298.15}^{\circ} = 109.5 \pm 5 \text{ kcal gfw}^{-1}$ . Thus, the results are in agreement with the direct measurements but are of less precision.

Using free-energy functions for the condensed phase of silicon and for gaseous monatomic silicon as already discussed, and the heat of formation adopted above, a normal boiling point of  $3565.77^{\circ}\text{K}$  has been calculated. The uncertainty in the boiling point is estimated to be  $\pm 100^{\circ}\text{K}$ .

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## 26. Strontium

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references for the elements can be found in sections VIII and IX, volume 2 of this work.

## 27. Tantalum

Elemental tantalum exists as a bcc A2-type structure with a lattice parameter of  $3.3026 \text{ \AA}$ .<sup>1</sup> Low-temperature heat-capacity measurements have been reported by several investigators.<sup>2-9</sup> The recent analysis of Kelley<sup>10</sup> gives  $S_{298.15}^{\circ} = 9.92 \pm 0.04 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , in agreement with Sterrett and Wallace;<sup>7</sup> the latter also give  $H_{298}^{\circ} - H_0^{\circ} = 1358 \text{ cal gfw}^{-1}$ . These values compare with the earlier values of  $S_{298.16}^{\circ} = 9.90 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  and  $H_{298}^{\circ} - H_0^{\circ} = 1358 \text{ cal gfw}^{-1}$  reported by Stull and Sinke.<sup>11</sup> In the present analysis, the recent Kelley<sup>10</sup> and Sterrett and Wallace<sup>7</sup> data for  $S_{298.15}^{\circ} = 9.92 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  and  $H_{298}^{\circ} - H_0^{\circ} = 1358 \text{ cal gfw}^{-1}$  are accepted.

High-temperature heat capacities have been measured by numerous workers. Pulse techniques have been used by Taylor and Finch<sup>12</sup> for the range  $100^{\circ}$  to  $3195^{\circ}\text{K}$ , by Lehman<sup>13</sup> from  $100^{\circ}$  to  $3200^{\circ}\text{K}$ , and by Rasor and McClelland.<sup>14</sup> Hoch and Johnston<sup>15</sup> used a drop technique for the range  $1089^{\circ}$  to  $2666^{\circ}\text{C}$  ( $1362^{\circ}$  to  $2939^{\circ}\text{K}$ ), while Fieldhouse et al<sup>16</sup> used a drop technique for the range  $841^{\circ}$  to  $1910^{\circ}\text{K}$ .

Earlier high-temperature heat-capacity data for tantalum have been summarized by Kelley,<sup>17</sup> who gives an equation of the form  $C_p^{\circ} = 6.31 + 0.40 \times 10^{-3}T - 0.32 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  for the range  $298^{\circ}$  to  $3000^{\circ}\text{K}$ .

For the present analysis, the equation of Kelley was accepted for the range  $298.15^{\circ}$  to  $950^{\circ}\text{K}$ . The data join smoothly at  $298.15$  with the low-temperature heat-capacity data. Above  $950^{\circ}\text{K}$ , a smooth curve joined with the Kelley data and was in good agreement with the data of Rasor and McClelland,<sup>14</sup> Lehman,<sup>13</sup> and Taylor and Finch,<sup>12</sup> for the range  $950^{\circ}$  to  $3270^{\circ}\text{K}$ . In this high-temperature region ( $950^{\circ}$  to  $3270^{\circ}\text{K}$ ), the final selected data are greater than given by the Kelley equation or that given by Hoch and Johnston.<sup>15</sup> On the other hand, it is less than the values given by Fieldhouse et al.<sup>16</sup>

For comparative purposes, various  $C_p^{\circ}$  values in  $\text{cal deg K}^{-1} \text{ gfw}^{-1}$  are presented on the following page.

Melting points of  $3253$ ,<sup>18</sup>  $3263$ ,<sup>18</sup>  $3269$ ,<sup>19</sup>  $3270$ ,<sup>11</sup> and  $3273^{\circ}\text{K}$  have been listed. For the present case, the value  $3270^{\circ}\text{K}$  has been accepted. A heat of fusion of  $6.7 \text{ kcal gfw}^{-1}$ , corresponding to an entropy of fusion of  $2.049 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , was accepted. This heat of fusion was an average of  $7.5 \text{ kcal gfw}^{-1}$  estimated by Stull and Sinke<sup>11</sup> and  $5.9 \text{ kcal gfw}^{-1}$  estimated by Kubaschewski and Evans.<sup>18</sup>

TABLE 16  
COMPARISON OF  $C_p^\circ$  VALUES OF Ta  
(cal deg K<sup>-1</sup> gfw<sup>-1</sup>)

Reference	T 1800°K	T 2800°K
This Analysis	7.190	9.309
Fieldhouse <u>et al</u> <sup>16</sup>	8.8	- - -
Rasor <u>et al</u> <sup>14</sup>	7.2 (avg)	9.0
Taylor and Finch <sup>12</sup>	7.328	9.048
Lehman <sup>13</sup>	7.401	9.228
Hoch and Johnston <sup>15</sup>	7.06	7.593
Stull and Sinke <sup>11</sup>	7.02	7.44
Kelley <sup>17</sup>	7.020	7.426

There are no reported phase transitions in the condensed state of tantalum.

For the liquid-phase heat capacity, an estimated value of  $C_p^\circ = 8.5 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$  was used.

Thermodynamic functions for the condensed phase were obtained by numerical integration of the smoothed heat capacity and other data already discussed.

Thermodynamic functions for the ideal monatomic gas were calculated, using the energy levels tabulated by Moore.<sup>20</sup> The data agreed with the incomplete table of an earlier publication.<sup>21</sup>

Vapor-pressure data for the range 2624° to 2948°K have been reported by Edwards, Johnston, and Blackburn.<sup>22</sup> Other data have been reported by Gebhardt, Seghezzi, and Keil,<sup>23</sup> Langmuir and Malter,<sup>19</sup> and Fiske.<sup>24</sup> Data from these four sources were analyzed by a Third-Law treatment, using free-energy functions calculated during the present analysis. Results are shown on the following page.

The data of Edwards et al<sup>22</sup> show the smallest deviation and are in very good agreement with the Langmuir-Malter data.<sup>19</sup> The recent work of Gebhardt<sup>23</sup> et al was based on measuring electrical resistance and changes in cross section of tantalum wire specimens. They had reported a heat of sublimation of 230 kcal/mole, using essentially a Second-Law analysis.

The present Third-Law analysis of the Gebhardt data yields a value of 189.936 kcal/mole for the heat of sublimation at 298°K, in relatively good agreement with the other reported data.

TABLE 17  
COMPARISON OF HEAT-OF-SUBLIMATION VALUES OF Ta

Reference	Year	Temperature Range	Number of Measurements	$\Delta H_{f298}^\circ$	Deviation
		°K			
Edwards <u>et al</u> <sup>22</sup>	1951	2624 to 2948	7	186.522	± 0.262
Langmuir <u>et al</u> <sup>19</sup>	1939	2000 to 3269	8	186.738	± 0.629
Fiske <sup>24</sup>	1942	2633 to 2850	7	181.821	± 0.981
Gebhardt <u>et al</u> <sup>23</sup>	1962	2900 to 3150	8	189.936	± 1.068
Average 186.254					

In making a final choice, the Edwards et al<sup>22</sup> data have been accepted because they show the smallest deviation and agree well with the Langmuir-Malter data and the average of the four different investigations.

Thus, the final selected value for the heat of sublimation at 298.15°K is  $\Delta H_{298.15}^\circ = 186.522 \text{ kcal gfw}^{-1}$ . The actual uncertainty of this value (as contrasted with the statistical deviation already quoted) is believed to be approximately ± 3 kcal; the estimate is based primarily on the range of values reported.

Using the data accepted thus far, a normal boiling point of 5706.65°K has been calculated. Although six significant figures are shown, the probable accuracy of this value is likely to be ± 200°K. The boiling point corresponds to  $\Delta H_{\text{vap}}^\circ = 181.223 \text{ kcal gfw}^{-1}$  and an entropy of vaporization at the boiling point of  $\Delta S_{\text{vap}}^\circ = 31.755 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ .

#### Supplement

A very recent reference to mass spectrometric vaporization studies of tantalum by Babeliowsky<sup>25</sup> was read too late for inclusion in the present analysis. He reported a heat of sublimation of only  $168.4 \pm 4 \text{ kcal gfw}^{-1}$ , which is considerably lower than the data accepted here. His experiment used tantalum wires, and he had to make emissivity corrections to accomplish a temperature measurement. Furthermore, his data could only be analyzed by Second Law methods since he did not measure absolute pressures. Therefore, in view of the agreement of the other data already presented, it is believed probable that these last data are in error.

Heat-capacity data for tantalum in the range 1200° to 2900°K have been reported by Kraftmakher.<sup>26</sup> He found that, for the range 1200° to 2000°K,  $C_p^\circ = 5.82 + 0.0068 T \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Above 2000°K, there was an additional term due to formation of vacancies. Lowenthal<sup>27</sup> reported heat-capacity data for the range 1256° to 2300°K.

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## 28. Technetium

### a. Crystal Structure and Melting Point

Elemental technetium was found to have a hexagonal close-packed, A3-type structure.<sup>1</sup> No evidence for other crystalline modifications was found<sup>2</sup> at pressures up to 100,000 kg/cm<sup>2</sup> except for a superconducting phase below 11.2°K.<sup>3</sup> A melting point of 2413° ± 20°K was reported<sup>4</sup> from what was described as a "preliminary" measurement. More recently, the melting point was measured to be 2473° ± 50°K.<sup>5</sup> The latter value was adopted herein.

### b. Thermodynamic Properties

#### 1) Heat of fusion

The entropy of fusion was assumed to be 2.300 e. u. This gave a heat of fusion of 5.688 kcal/gfw. An uncertainty of ± 1.000 kcal/gfw was assigned to the heat of fusion.

#### 2) Entropy and heat content at 298.15°K

$S_{298}^{\circ}$  for technetium was estimated to be 9.0 e. u. in NBS Circular 500,<sup>6</sup> 8.0 e. u. by Brewer,<sup>7</sup> and 7.4 e. u. by Cobble.<sup>8</sup> For the present compilation, Brewer's<sup>7</sup> estimate was adopted with an uncertainty of ± 0.500 e. u. as recommended by Kelley and King.<sup>9</sup> The adopted value appeared to be the most consistent with  $S_{298}^{\circ}$  values for neighboring elements in the periodic table.  $H_{298} - H_0$  was estimated to be 1.230 kcal/gfw.

#### 3) High-temperature heat capacity

Experimental measurements were not available. Kelley<sup>10</sup> gave an equation for the high-temperature heat capacity of technetium in cal/°K gfw based on heat-content estimates by Brewer;<sup>7</sup> i. e.,

$$C_p^{\circ} = 5.200 + 2.000 \times 10^{-3} T \quad . \quad (\text{IVA28-1})$$

This equation was adopted herein.

The heat capacity of liquid technetium was estimated to be 10.000 cal/°K gfw.

#### 4) Standard heat of formation of the gas at 298.15°K

The estimate for  $\Delta H_{f298}^{\circ}$  of 155.000 kcal/gfw by Stull and Sinke<sup>11</sup> was adopted herein and assigned an uncertainty of  $\pm 5.000$  kcal/gfw. This estimate was based on vapor-pressure estimates of Brewer.<sup>7</sup>

The normal boiling point and the corresponding heat of vaporization were calculated to be  $4840.07^{\circ} \pm 500^{\circ}\text{K}$  and  $139.871 \pm 13.2$  kcal/gfw, respectively.

#### 5) Ideal gas

The thermodynamic functions of the ideal monatomic gas of Tc reported earlier<sup>12</sup> were retained.

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## 29. Thorium

### a. Crystal Structure, Transition Point, and Melting Point

Elemental thorium was found to have a face-centered cubic, A1-type structure from room temperature to 1360°C and a body-centered cubic A2 structure<sup>1-3</sup> from 1360°C to the melting point. The transition point and, in particular, the melting point had been found to be very sensitive to the kind and amount of impurities. Summaries of the earlier and frequently discordant results were found in numerous review publications on thorium.<sup>4-7</sup> Kelley<sup>8</sup> and Stull and Sinke<sup>9</sup> adopted an  $\alpha$ - $\beta$  transition temperature of 1400°C<sup>1</sup> and a melting point of 1695°C from earlier measurements of Chiotti.<sup>10</sup> In 1954, Chiotti<sup>1</sup> recommended a melting point of 1750°C. Later, he quoted unpublished studies of Chiotti and Gill<sup>11</sup> as leading to a value of 1360°C for the transition point and of 1755°C for the melting point. The latter temperatures were adopted for the present compilation. The transition temperature had also been determined to be  $1363^\circ \pm 10^\circ\text{C}$  by McMasters and Larsen<sup>12</sup> and to be  $1330^\circ \pm 20^\circ\text{C}$  by Wilson, Austin, and Schwartz.<sup>3</sup> Bentle<sup>13</sup> reported a plot of phase data which seemed to place the  $\alpha$ - $\beta$  transition around 1350' to 1360°C.

### b. Thermodynamic Properties

#### 1) Heat of transition and fusion

The heats of transition and fusion of thorium had not been measured. Although no thermal arrest was noted by some observers on cooling massive amounts of liquid thorium, such an arrest had been observed by Carlson<sup>4</sup> at 1626°C. The rapid solidification of liquid thorium on casting had been cited as evidence for an unusually low heat of fusion.<sup>4</sup> However, phase data for some thorium systems had been analyzed<sup>4</sup> to indicate a heat of fusion of the order of 4 kcal/gfw. For the present compilation, the estimates of Stull and Sinke<sup>9</sup> of 0.4 e. u. for the entropy of transition and 1.9 e. u. for the entropy of fusion were adopted. The corresponding heats of transition and fusion were  $0.653 \pm 0.200$  kcal/gfw and  $3.853 \pm 1.000$  kcal/gfw, respectively.

#### 2) Entropy and heat content at 298.15°K

The low-temperature heat capacity of thorium was measured by Smith and Wolcott<sup>14</sup> and by Griffel and Skochdopole.<sup>15</sup> Griffel and Skochdopole calculated  $S_{298}^\circ$  to be 12.760 e. u. and  $H_{298}^\circ - H_0^\circ$  to be 1.556 kcal/gfw from their data. Kelley and King<sup>16</sup> gave an uncertainty of  $\pm 0.2$  e. u. to the entropy value. This relatively

large uncertainty was due primarily to an uncertainty in the entropy below 20°K, which was in turn due to differing values of the electronic heat capacity from the data of Smith and Wolcott,<sup>14</sup> and Griffel and Skochdopole.<sup>15</sup> Clusius and Franzosini<sup>17</sup> attributed the differing electronic heat capacities to differing sample purity.

Thorium has been found to be a superconductor below 1.4°K.<sup>18,19</sup>

### 3) High-temperature heat content

The high-temperature heat content of thorium was measured by Jaeger and Veenstra,<sup>20</sup> and the high-temperature heat capacity was measured by Wallace,<sup>21</sup> and Mitkina.<sup>22</sup> The measurements of Jaeger and Veenstra<sup>20</sup> were made on metal containing 6.04-percent ThO<sub>2</sub>. A correction to the observed heat content was therefore necessary. The tabulations of Kelley,<sup>8</sup> and Stull and Sinke<sup>9</sup> were based on these corrected data. The tabulated data did not reproduce the corrected data of Jaeger and Veenstra<sup>20</sup> particularly well, probably because the last were modified further to give the heat capacity at 298.15°K from the low-temperature data of Griffel and Skochdopole.<sup>15</sup> However, neither the corrected data nor their modification by Kelley<sup>8</sup> joined smoothly with the low-temperature results. The corrected data gave a heat capacity at 298.15°K that was much too large, and their modification gave a temperature coefficient of the heat capacity near room temperature at variance with the low-temperature measurements.

The high-temperature heat-capacity data of Wallace<sup>21</sup> were obtained by a pulse-heating method on 10-mil thorium wires. These data joined smoothly with the low-temperature data. Above a temperature of approximately 500°K, a contribution to the heat capacity in addition to the contributions of lattice vibrations  $C_p - C_v$  and the electronic heat capacity was observed which fitted a Schottky-type equation. This excess was attributed by Wallace<sup>21</sup> to thermal excitation of electrons to a narrow energy band above or below the Fermi level, and not to defect formation. A similar interpretation was made<sup>23</sup> of the heat-capacity measurements on uranium.<sup>24</sup> The results of Wallace<sup>21</sup> were adopted for this compilation and extrapolated to the  $\alpha$ - $\beta$  transition at 1633°K. These data in cal/°K gfw were represented by the following pair of equations over the temperature ranges of 298° to 800°K and 800° to 1633°K, respectively:

$$C_p^\circ = 5.773 + 2.548 \times 10^{-3} T \quad , \quad (\text{IVA29-1})$$

$$C_p^\circ = 5.553 + 4.928 \times 10^{-3} T - 4.703 \times 10^{-6} T^2 + 2.590 \times 10^{-9} T^3 \quad .$$

(IVA29-2)

The technique used by Mitkina<sup>22</sup> gave a heat capacity that was too low at room temperature and increased too rapidly with temperature to 700°K.

The estimate of 11.000 cal/°K gfw for the heat capacities of both  $\beta$ -Th and liquid thorium made by Kelley,<sup>8</sup> and Stull and Sinke<sup>9</sup> was adopted herein.

#### 4) Standard heat of formation of the gas at 298.15°K

Thorium vapor-pressure data had been reported by Zwikker,<sup>25</sup> Andrews,<sup>26</sup> deBoer,<sup>27</sup> Darnell, McCollum, and Milne,<sup>28</sup> and Goldwater and Danforth.<sup>29</sup>

Most tabulations of thorium vapor pressures were taken from Brewer,<sup>30</sup> who combined the data of Zwikker,<sup>25</sup> and deBoer.<sup>27</sup> Dushman<sup>31</sup> and Lofthus<sup>32</sup> also gave compilations based on Zwikker's<sup>25</sup> results. The original vapor-pressure data were not given by Zwikker,<sup>25</sup> and deBoer,<sup>27</sup> so that it was possible to calculate only a rough value of the standard heat of formation of the gas with the thermodynamic functions given herein. If the various representations of these early data were all used, the heat of sublimation at 298.15°K would vary from 130 to 140 kcal/gfw.

The data of Andrews<sup>26</sup> gave a heat of formation that was much too high, probably due to the evaporation of ThO<sub>2</sub> rather than thorium.

For the present compilation, the vapor-pressure data of Darnell, McCollum, and Milne<sup>28</sup> were adopted. A standard heat of formation of the gas at 298.15°K of  $137.700 \pm 1.000$  kcal/gfw was derived by the Third-Law method. The last authors discussed the high evaporation rates from thorium containing ThO<sub>2</sub> due to the formation of ThO(g) from the reaction of thorium with ThO<sub>2</sub>.

The smoothed evaporation-rate data of Goldwater and Danforth<sup>29</sup> gave a heat of formation that was 10 or more kcal/gfw too low and quite temperature-dependent.

The normal boiling point and associated heat of vaporization were calculated to be  $5060.26^\circ \pm 440^\circ\text{K}$  and  $122.765 \pm 15.060$  kcal/gfw, respectively. This boiling point was  $560^\circ\text{K}$  higher than the previous estimate of Brewer.<sup>30</sup>

5) Thermodynamic functions of ideal monatomic gas

The thermodynamic functions of ideal monatomic thorium gas were calculated from the energy levels given by Zalubas.<sup>33</sup> The functions so calculated must be regarded as tentative since the analysis of the thorium spectrum was incomplete.<sup>33</sup>

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### 30. Titanium

In the earlier report,<sup>1</sup> the analysis and thermodynamic tables for titanium reference state and the ideal monatomic gas have been presented. This work is utilized in the present project. Some more recent work which could not be analyzed includes crystal studies by Takeuchi et al,<sup>2</sup> and Amonenko et al,<sup>3</sup> heat-capacity data by Holland,<sup>4</sup> Fieldhouse and Lang,<sup>5</sup> Serebrennikov and Geld,<sup>6</sup> Stalinski and Bieganski,<sup>7</sup> and Starke et al,<sup>8</sup> and vaporization studies by Kuzmin and Palatnik,<sup>9</sup> Schram,<sup>10</sup> and Hanlin.<sup>11</sup> Transitions in titanium at high pressure have been discussed by Jayaraman et al.<sup>12</sup>

#### Supplement

Holland<sup>4</sup> has measured the specific heat of metallic titanium in the range 600° to 1345°K. The increase in specific heat to 1.7 times the Dulong and Petit value is interpreted as an effect of anharmonic terms in the potential of atomic oscillators.

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### 31. Tungsten

For a discussion of this element, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any references to the element can be found in sections VIII and IX, volume 2 of this work.

### 32. Uranium

#### a. Crystal Structure, Transition Points, and Melting Point

Elemental uranium exists in three modifications ( $\alpha$ ,  $\beta$ , and  $\gamma$  phases) below its melting point. A number of measurements of the  $\alpha$  -  $\beta$  and  $\beta$  -  $\gamma$  transition temperatures have been made. Data from several of the more recent measurements are shown in table 18. In most cases, the transition temperatures have been obtained from thermal arrest data for several properties which are functions of phase and temperature. Where data are obtained from both heating and cooling cycles, a considerable hysteresis effect is noted.

The most reliable data appear to be those of Blumenthal,<sup>1</sup> who made a careful study of the hysteresis effect upon transition temperatures in uranium. The  $\alpha$  -  $\beta$  and  $\beta$  -  $\gamma$  transition temperatures are, therefore, taken to be  $940^\circ \pm 1.3^\circ\text{K}$  and  $1048^\circ \pm 1.6^\circ\text{K}$ , respectively.

The  $\alpha$  phase is thought to exist from  $0^\circ$  to  $940^\circ\text{K}$  with the reservation that an anomaly has been reported at  $42^\circ \pm 1^\circ\text{K}$ . Jacobson and Warren<sup>2</sup> first demonstrated that the  $\alpha$  phase is orthorhombic, and this has been confirmed by Lukesh.<sup>3</sup> Since the original studies, several other workers have reported values for the room-temperature lattice constants.<sup>4, 5</sup> The most recent values are those obtained by Cooper<sup>6</sup> with very high purity uranium. Cooper's lattice constants for  $\alpha$  uranium at  $25^\circ\text{C}$  are

- a =  $2.81785 \pm 0.00005 \text{ \AA}$ ,
- b =  $5.85801 \pm 0.0006 \text{ \AA}$ , and
- c =  $4.91553 \pm 0.00006 \text{ \AA}$ .

TABLE 18

THE  $\alpha$  -  $\beta$  AND  $\beta$  -  $\gamma$  TRANSITION TEMPERATURES OF URANIUM METAL

$\alpha$ - $\beta$	$\beta$ - $\gamma$	Reference
$^\circ\text{K}$	$^\circ\text{K}$	
$940 \pm 1.3$	$1048 \pm 1.6$	1
$930^\circ$ to $955^\circ$	$1027^*$ to $1047^{**}$	7
$930^{**}$	$1040^{**}$	8
$929.5^*$ to $938.5^{**}$	$1039.5^*$ to $1044.0^{**}$	9
$918^*$ to $940^{**}$	$1037^*$ to $1045^{**}$	10
$935 \pm 3$		11

\*Cooling cycle (thermal arrest).

° Heating cycle (thermal arrest).

The  $\alpha$  structure may be considered as made up of corrugated layers, with the layers parallel to the a-c plane and the corrugations parallel to the a-axis. Other important details of the  $\alpha$  structure are discussed by Holden.<sup>12</sup>

Abnormalities in several properties of  $\alpha$  uranium near 42°K have been observed,<sup>13, 14</sup> and a close analysis of the heat-capacity data of Flotow and Lohr<sup>15</sup> reveals anomalous behavior between 42° and 44°K. Fisher and Meskimin<sup>16</sup> have studied the elastic moduli of  $\alpha$  uranium in the low-temperature range by the use of ultrasonic pulse techniques and also, have obtained evidence for a solid-state transition. They postulate that there is phase instability at 42.5°K which results from a change in the nature of some of the interatomic bonds.

The structure of the  $\beta$  phase has been demonstrated by Tucker<sup>17-21</sup> to be tetragonal with

$$a = b = 10.52 \text{ \AA} \text{ and}$$

$$c = 5.57 \text{ \AA},$$

on the basis of his work with quenched uranium chromium alloys. Thewlis<sup>22-24</sup> has given lattice parameters (at 990°K) of

$$a = b = 10.759 \text{ \AA} \text{ and}$$

$$c = 5.656 \text{ \AA},$$

on the basis of powder studies. Details of the bond arrangement of uranium are not clear. It appears that resolution of its detailed structure will have to await single-crystal X-ray analysis at high temperatures.

Thewlis,<sup>22</sup> and Wilson and Rundle,<sup>25</sup> have reported that  $\gamma$  uranium has a body-centered-cubic (bcc) structure. Wilson and Rundle obtained  $a = 3.487 \text{ \AA}$  at 800°C (1073°K) and  $a = 3.474 \text{ \AA}$  at 25°C (298°K). Thewlis obtained  $a = 3.525 \text{ \AA}$  at 805°C (1078°K). The most recent work is that of Klepfer and Chiotti<sup>26</sup> in which a value of  $a = 3.538 \text{ \AA}$  has been obtained at 800°C (1073°K).

The melting point of  $\gamma$  uranium to form the liquid has been reported by a number of workers. The values obtained in the last 15 years are given on the following page.

## THE MELTING POINT OF URANIUM

Temperature °K	Reference
1405.5 ± 0.8	1
1405 ± 10	27
1407	7
1406	8
1406 ± 2	28
1403	9

Holden<sup>12</sup> accepts the value of Baumrucker and Chiswick<sup>9</sup> (1403°K) on the basis of the high purity of their uranium sample. In this compilation, the melting point is being taken as 1406° ± 2°K. The basis for this selection is the consistency of other workers' data and the work of Blumenthal<sup>1</sup> with high-purity uranium. Holden's selection of a lower value for the melting point on the basis of sample purity does not seem reasonable since the apparent melting point would be depressed by most impurities.

### b. Thermodynamic Properties

#### 1) Heat capacity, heat of formation, and fusion

At low temperatures (5° to 300°K), the heat-capacity data of Flotow and Lohr<sup>15</sup> are taken to be the most reliable since these workers have been able to use very pure uranium. The data selected, and that of Jones, Gordon, and Long,<sup>29</sup> are, however, in quite good agreement. The low-temperature data have been joined smoothly to the high-temperature data (300° to 940°K) of Ginnings and Corruccini.<sup>30</sup> The high-temperature data of Ginnings and Corruccini are in fair agreement with those of Kelley<sup>31</sup> except near the  $\alpha$  -  $\beta$  transition temperature. There seems to be little basis for selection between the two sets of data, and it appears that further work should be done to clarify this situation.

The heat capacities of the  $\beta$  and  $\gamma$  phases are taken to be 10.15 and 9.15 cal/°K gfw, respectively.<sup>30</sup> Several other investigators have reported a constant heat capacity for the  $\beta$  and  $\gamma$  ranges.<sup>6,11</sup> This seems doubtful and should probably be checked more closely.

The heats for the  $\alpha - \beta$  and  $\beta - \gamma$  transitions have been taken to be 685 and 1120 cal/gfw, respectively, and the heat of melting as 4700 cal/gfw on the basis of the work of Rauh and Thorn.<sup>32</sup>

2) Standard heat of formation of the gas at 298.15°K

Uranium vapor-pressure data for liquid uranium near 2000°K have been reported by Rauh and Thorn<sup>32</sup> and by DeMaria, Burns, Drowart, and Inghram.<sup>33</sup> There is some doubt about both sets of data since there is a possibility that oxygen interfered with the work of Rauh and Thorn, and since DeMaria et al used uranium saturated with molybdenum and likely in contact with solid  $\text{UO}_2$ . The data of Rauh and Thorn have been selected for this compilation on the basis of arguments recently presented by Ackermann, Rauh, and Thorn.<sup>34</sup> The vapor-pressure data discussed above have been used along with the free-energy function data presented in the uranium reference state table to obtain a standard heat of formation of the gas at 298.15°K of 117.06 kcal/gfw and a boiling point of 4124°K.

3) Thermodynamic functions of the ideal monatomic gas

The thermodynamic functions of ideal monatomic uranium gas have been calculated from a set of 416 energy levels determined by Blaise.<sup>35</sup> The functions so obtained must be regarded as tentative since the uranium spectrum is incomplete.

4) Uncertainty estimates

The uncertainty estimates for the reference state are taken from the original reference where possible. At higher temperatures, the uncertainty estimates have been arbitrarily made. Uncertainty estimates (where given) for the ideal gas table are obtained by assuming an uncertainty of  $\pm 0.05 \text{ cm}^{-1}$  for the term values.

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### 33. Vanadium

#### a. Crystal Structure and Melting Point

According to Hansen and Anderko,<sup>1</sup> elemental vanadium has a bcc structure of the A2 type. Its lattice parameter is 3.039 Å. There are no known transitions, and hence vanadium retains its cubic structure to the melting point.

A large number of values have been reported for the melting-point temperature; some of them are listed below. For the present calculations, a value of 2190°K was accepted.

MELTING POINTS OF VANADIUM

Reference	T (°K)
McPherson <sup>2</sup>	2193
Oriani and Jones <sup>3</sup>	2192 ± 2
Stull and Sinke <sup>4</sup>	2190 ± 10
Hansen and Anderko <sup>1</sup> Adenstedt <u>et al</u> <sup>5</sup>	2173 ± 25
Rostoker <sup>6</sup> Leslie and Rickett <sup>7</sup>	2173
Storms and McNeal <sup>8</sup>	2161
Williams <sup>9</sup> Wilhelm <u>et al</u> <sup>10</sup>	2133

#### b. Thermodynamic Properties

##### 1) Heat of fusion

Since no experimental values were available for the heat of fusion, an estimated value of 4200 cal gfw<sup>-1</sup> was used, based on Stull and Sinke.<sup>4</sup> An uncertainty of ± 1000 cal gfw<sup>-1</sup> was assigned, giving as the adopted value 4200 ± 1000 cal gfw<sup>-1</sup>.

## 2) Entropy and heat content at 298.15°K

From the low-temperature (50° to 300°K) data of Anderson,<sup>11</sup> a value of  $S_{298}^{\circ} = 7.01 \pm 0.10 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$  has been calculated by Stull and Sinke.<sup>4</sup> More recently, Clusius, Franzosini, and Piesbergen<sup>12</sup> from measurements between 10° and 273°K derived  $S_{298.15}^{\circ} = 6.85 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ . Also, Bieganski and Stalinski<sup>13</sup> found from data between 24° and 340°K that  $S_{298.15}^{\circ} = 6.88 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  with  $H_{298}^{\circ} - H_0^{\circ} = 1121.9 \text{ cal gfw}^{-1}$ . For the present work, the most recent data from Bieganski and Stalinski have been used since they show good agreement with the earlier data. An uncertainty of  $\pm 0.05 \text{ cal gfw}^{-1}$  is assigned.

## 3) High-temperature heat content

Stull and Sinke<sup>4</sup> had used the data of Jaeger and Veenstra.<sup>14</sup> Kelley<sup>15</sup> has also used Jaeger and Veenstra's<sup>14, 16</sup> data for the range 273° to 1828°K. Thus, Kelley derives a heat-capacity equation of the type,

$$C_p^{\circ} = 4.90 + 2.58 \times 10^{-3}T + 0.20 \times 10^{-5}T^2 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}. \quad (\text{IVA33-1})$$

More recently, Golutvin and Kozlovskaya<sup>17</sup> have obtained heat-content data for the range 298° to 1485°K. Their tabulated enthalpy contents are in general agreement with the Kelley<sup>15</sup> data, showing a maximum deviation of about 5 percent at the highest temperature; i. e., 1485°K, the heat content reported by Golutvin and Kozlovskaya being greater. Their heat-capacity equation was

$$C_p^{\circ} = 7.848 + 0.298 \times 10^{-3}T - 232843 T^{-2} \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}. \quad (\text{IVA33-2})$$

Comparisons of thermodynamic data calculated from the Golutvin and Kozlovskaya<sup>17</sup> equation and the Kelley<sup>15</sup> equation are made in table 19. It is seen that the maximum deviation in free-energy functions is still only  $0.4 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$  at 2000°K. This temperature already exceeds the range of experimental measurements for both sets of data.

Additional high-temperature (1500° to 2400°F, 1088° to 1588°K) heat-capacity data for vanadium have been obtained by Boggs and co-workers.<sup>18, 19</sup> They obtained data by both a "manual" and an "automatic" method. In the latter case, they obtained relatively good agreement with data from Kelley.<sup>20</sup> These earlier Kelley data are essentially the same as appear in his more recent publication.<sup>15</sup> Fieldhouse and Lang<sup>21</sup> have measured the heat capacity of vanadium for the range 403° to 2950°F (478.8° to 1893°K). Their equation has the form

$$C_p^\circ = 0.110 + 0.0028 \times 10^{-2} t \text{ Btu degF}^{-1} \text{ lb}^{-1} \quad (\text{IVA33-3})$$

where  $t$  is in  $^\circ\text{F}$ . The actual measured heat content at the highest temperature ( $1893^\circ\text{K}$ ) is 12.567 kcal/mole which is only slightly larger (1.4 percent) than the Kelley value of 12.380 kcal/mole. Thus, the various data appear to be in moderately good agreement; and for the present calculations, the Kelley<sup>15</sup> equation is used.

TABLE 19

COMPARISON OF VANADIUM THERMODYNAMIC DATA

T	Reference	$C_p^\circ$	$S_T^\circ$	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$
$^\circ\text{K}$		$\text{cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$	$\text{cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$	$\text{cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$	$\text{kcal gfw}^{-1}$
298.15	Golutvin <sup>17</sup>	5.317	6.88	6.88	0.0
	Kelley <sup>15</sup>	5.894	6.88	6.88	0.0
1000	Golutvin <sup>17</sup>	7.913	15.393	10.297	5.096
	Kelley <sup>15</sup>	7.500	14.723	10.062	4.661
2000	Golutvin <sup>17</sup>	8.386	21.044	14.407	13.274
	Kelley <sup>15</sup>	10.065	20.707	13.986	13.441

For the liquid phase, a heat capacity of  $9.5 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$  has been utilized, following the choice of Kelley<sup>15</sup> and Stull and Sinke.<sup>4</sup>

4) Standard heat of formation of the gas at  $298.15^\circ\text{K}$

The only vapor-pressure data available for vanadium have been reported by Edwards, Johnston, and Blackburn<sup>22</sup> for the temperature range ( $1666^\circ$  to  $1882^\circ\text{K}$ ). Using their reported pressures with free-energy functions from the present studies for monatomic vanadium gas and the condensed phase, a heat of formation of gas at 298.15 has been calculated as  $\Delta H_{298.15}^\circ = 123.010 \pm 0.127 \text{ kcal gfw}^{-1}$ . This is in good agreement with the value of  $122.750 \text{ kcal gfw}^{-1}$  found by Stull and Sinke,<sup>4</sup> and  $123.17 \text{ kcal gfw}^{-1}$  from Hultgren<sup>23</sup> and Honig.<sup>24</sup> In the preceding analysis, the  $\pm 0.127$  reflects only

the precision of the data. As far as the true uncertainty of these data is concerned, it is apt to be considerably larger. In the absence of other determinations, it is suggested that the uncertainty is  $\pm 4$  kcal gfw<sup>-1</sup>. Hence, the heat of formation is considered to be  $123.010 \pm 4$  kcal gfw<sup>-1</sup>.

The above data lead to a normal boiling point of 3647.68°K, again in good agreement with Stull and Sinke's value of 3650°K.

#### 5) Ideal gas

Thermodynamic functions for the ideal gas reported earlier<sup>25</sup> were utilized to complete the ideal monatomic gas table.

#### Supplement

Vaporization data have been reported by Saxer.<sup>26</sup>

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## 34. Yttrium

### a. Physical Properties

#### 1) Crystal structure, transition point, and melting point

At room temperature, elemental yttrium has a hexagonal close-packed (hcp) structure,<sup>1</sup>  $a_0 = 3.6474 \text{ \AA}$  and  $c_0 = 5.7306 \text{ \AA}$ . This structure persists up to about  $1485^\circ\text{C}$ , where there is a transformation to the body-centered structure.<sup>2-4</sup> Spedding *et al*<sup>5</sup> give the following equations for the temperature dependence of the lattice parameter  $a$ , the parameter  $c$ , the ratio  $c/a$ , the atomic volume  $v$ , and the density  $d$ . (All equations are applicable up to  $897^\circ\text{C}$  and  $t$  is in  $^\circ\text{C}$ .)

$$a = 3.6451 + 2.76 \times 10^{-5}t - 1.92 \times 10^{-8}t^2 + 2.16 \times 10^{-11}t^3 (\text{\AA}), \quad (\text{IVA34-1})$$

$$c = 5.7305 + 12.40 \times 10^{-5}t - 3.13 \times 10^{-8}t^2 + 2.92 \times 10^{-11}t^3 (\text{\AA}), \quad (\text{IVA34-2})$$

$$c/a = 1.5722 + 2.21 \times 10^{-5}t - 0.09 \times 10^{-8}t^2 - 0.09 \times 10^{-11}t^3, \quad (\text{IVA34-3})$$

$$v = 19.86 + 73 \times 10^{-5}t - 32 \times 10^{-8}t^2 + 3 \times 10^{-11}t^3 (\text{cm}^3/\text{gfw}), \text{ and } (\text{IVA34-4})$$

$$d = 4.478 - 1.68 \times 10^{-5}t + 8.1 \times 10^{-8}t^2 - 7.9 \times 10^{-11}t^3 (\text{gm/cm}^3). \quad (\text{IVA34-5})$$

Herrmann *et al*<sup>6</sup> report a melting point of  $1550^\circ \pm 5^\circ\text{C}$  for vacuum-distilled metal. Nolting *et al*<sup>7</sup> report two melting points. For a specimen obtained by lithium reduction of the anhydrous chloride, the melting point is given as  $1525^\circ \pm 10^\circ\text{C}$ , while for a specimen prepared by the intermediate alloy method of Carlson *et al*,<sup>8</sup> the melting point is given as  $1540^\circ \pm 10^\circ\text{C}$ . Habermann<sup>3</sup> reports  $1510^\circ\text{C}$  and Eash<sup>2</sup> reports  $1515^\circ\text{C}$ , while Berg<sup>4</sup> reports  $1530^\circ\text{C}$ . The melting point here adopted is  $1530^\circ \pm 15^\circ\text{C}$  ( $1803^\circ\text{K}$ ). Previous compilers,<sup>9,10</sup> presumably following Thompson *et al*,<sup>11</sup> had estimated the melting point as  $1773^\circ\text{K}$ .

#### 2) Mechanical properties

The elastic parameters of polycrystalline yttrium have been measured by Smith *et al*,<sup>12</sup> but these results are superseded by the extended study of yttrium single crystals over the range  $4.2^\circ$  to  $400^\circ\text{K}$  reported by Smith and Gjevne.<sup>13</sup> Averaging the single crystalline elastic constants at room temperature gives the following parameters:



Parameter	Property
Shear Modulus	$\mu = 2.55 \times 10^{11}$ dynes/cm <sup>2</sup>
Young's Modulus	$\gamma = 6.36 \times 10^{11}$ dynes/cm <sup>2</sup>
Poisson's Ratio	$\sigma = 0.25$
Compressibility	$\beta = 2.46 \times 10^{-6}$ cm <sup>2</sup> /kg

Bernstein and Smith<sup>14</sup> have given a theoretical calculation of the compressibility as  $2.69 \times 10^{-6}$  cm<sup>2</sup>/kg.

From their X-ray work, Spedding et al<sup>5</sup> report at 400°C a thermal expansion coefficient along the a-axis of  $6.2 \times 10^{-6}$  degC<sup>-1</sup>, along the c-axis  $19.7 \times 10^{-6}$  degC<sup>-1</sup>, and an average linear coefficient of  $10.8 \times 10^{-6}$  degC<sup>-1</sup>.

## b. Thermodynamic Properties

### 1) Heat of transition

The heat of transition of yttrium at 1485°C has been measured<sup>4</sup> at the Ames Laboratory and found to be  $1189 \pm 46$  cal gfw<sup>-1</sup>. The corresponding entropy change is  $0.6763$  cal°K<sup>-1</sup>gfw<sup>-1</sup>.

### 2) Heat of fusion

The heat of fusion is  $2732 \pm 25$  cal/gfw,<sup>4</sup> corresponding to an entropy change of  $1.511$  cal°K<sup>-1</sup>gfw<sup>-1</sup>. The sum of the entropy of transition and the entropy of fusion is  $2.187$  cal°K<sup>-1</sup>gfw<sup>-1</sup>, which is close to the value of  $2.3$  cal°K<sup>-1</sup>gfw<sup>-1</sup> previously adopted by Kelley<sup>9</sup> and Stull and Sinke<sup>10</sup> for the entropy of fusion.

### 3) Heat capacity at low temperatures

The heat capacity at liquid helium temperatures has been measured by Montgomery and Pells,<sup>15</sup> who report a Debye  $\theta$  of  $300 \pm 10^\circ\text{K}$  and a  $\gamma$ -coefficient of  $10.2 \pm 0.1$  millijoules/gfw (°K)<sup>2</sup>. The heat capacity over the range 15 to 350°K has been measured by Jennings et al,<sup>16</sup> who find  $\theta_D = 214^\circ\text{K}$  and  $\gamma = 8.5$  millijoules/gfw (°K)<sup>2</sup>. At  $298.15^\circ\text{K}$ ,  $C_p^\circ = 26.52$  millijoules/gfw °K ( $6.338$  cal/gfw °K), and at  $340^\circ\text{K}$ ,  $C_p^\circ = 26.92$  ( $6.434$  cal degK<sup>-1</sup>gfw<sup>-1</sup>). The actual room-temperature heat capacity is thus above that ( $6.01$ ) estimated by Stull and Sinke<sup>10</sup> and below that ( $6.45$ ) estimated by Lebedev.<sup>17</sup>

#### 4) Entropy and enthalpy at 298.15 °K

The standard entropy found by Jennings et al.<sup>16</sup> is  $S_{298.15}^{\circ} = 44.476$  joules/gfw°K ( $10.630 \text{ cal}^{\circ}\text{K}^{-1}\text{gfw}^{-1}$ ) which is somewhat lower than the estimate of  $11.0 \text{ cal}^{\circ}\text{K}^{-1}\text{gfw}^{-1}$  given by Brewer,<sup>18</sup> and adopted by Kelley and King,<sup>19</sup> and by Stull and Sinke.<sup>10</sup> The standard enthalpy as calculated by Jennings et al.<sup>16</sup> is  $(H_{298}^{\circ} - H_0^{\circ}) = 5964.49$  joules/gfw or  $1425.5 \text{ cal gfw}^{-1}$ . The free-energy function  $(F_{298}^{\circ} - H_0^{\circ})/T$  at 273.15°K is  $-22.747 \text{ joules degK}^{-1}\text{gfw}^{-1}$  or  $-5.436_6 \text{ cal}^{\circ}\text{K}^{-1}\text{gfw}^{-1}$ .

#### 5) High-temperature heat capacity and enthalpy

In the absence of experimental data, Kelley<sup>9</sup> estimated the thermochemical behavior above room temperature. He gave the equations

$$H_T^{\circ} - H_{298.15}^{\circ} = 5.72 T + 0.50 \times 10^{-3} T^2 - 1750 \text{ cal gfw}^{-1}, \text{ and} \quad (\text{IVA34-6})$$

$$C_p^{\circ} = 5.72 + 100 \times 10^{-3} T \text{ cal gfw}^{-1} \text{ deg K}^{-1} \quad (\text{IVA34-7})$$

as being applicable to the solid, and the equations

$$H_T^{\circ} - H_{298.15}^{\circ} = 8.00 T - 120 \text{ cal gfw}^{-1}, \text{ and} \quad (\text{IVA34-8})$$

$$C_p^{\circ} = 8.00 \text{ cal degK}^{-1} \text{ gfw}^{-1}. \quad (\text{IVA34-9})$$

as being applicable to the liquid to 3000°K. The tables given by Stull and Sinke<sup>10</sup> are based on these equations. It is seen that the first set of equations is not in agreement with the work of Montgomery and Pells<sup>15</sup> and Jennings et al.,<sup>16</sup> the temperature coefficient is much too low and the heat capacity at room temperature predicted by the equation is also too low.

Gschneidner<sup>20</sup> attempted to correct the linear coefficient and proposed the equation

$$C_p^{\circ} = 6.13 + 1.5 \times 10^{-3} t, t \text{ in } ^{\circ}\text{C}, \quad (\text{IVA34-10})$$

or

$$C_p^{\circ} = 5.72 + 1.5 \times 10^{-3} T. \quad (\text{IVA34-11})$$

This still is in disagreement with the room-temperature results of Jennings et al.<sup>16</sup> An obvious modification would be  $C_p^{\circ} = 6.31 + 1.5 \times 10^{-3} t \text{ cal deg C}^{-1} \text{ gfw}^{-1}$ .

All of the above work is superseded by Berg's<sup>4</sup> recent measurements, which are here regarded as definitive. Berg represents the enthalpy increment from 0°C as follows:

Range 0° to 1485°C

$$H_t^\circ - H_{298.15}^\circ = 6.310t + 7.733 \times 10^{-4}t^2 + 5.164 \times 10^{-8}t^3 \quad (\text{IVA34-12})$$

average deviation  $\pm$  0.29 percent.

Range 1485° to 1530°C

$$H_t^\circ - H_{298.15}^\circ = 8.371t + 1.1 \quad (\text{IVA34-13})$$

average deviation  $\pm$  0.11 percent

Liquid range

$$H_t^\circ - H_{298.15}^\circ = 10.303t - 222.2. \quad (\text{IVA34-14})$$

The corresponding heat-capacity equations are

$$C_p^\circ = 6.310 + 15.466 \times 10^{-4}t + 15.492 \times 10^{-8}t^2 \text{ cal}^\circ\text{C}^{-1}\text{gfw}^{-1} \quad (\text{IVA34-15})$$

or

$$C_p^\circ = 5.899 + 1.4 \times 10^{-3}T + 15.492 \times 10^{-8}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1} \quad (\text{IVA34-16})$$

for 273.15° to 1758°K,

$$C_p^\circ = 8.371 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1} \quad (\text{IVA34-17})$$

for 1758° to 1803°K,

and

$$C_p^\circ = 10.303 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1} \quad (\text{IVA34-18})$$

for the liquid. This last value was assumed constant to the boiling point of 3605°K.

## 6) Vapor pressure, heat of sublimation, and boiling point

The vapor pressure as a function of temperature has been measured by Ackermann and Rauh<sup>21</sup> and by Karelin et al.<sup>22</sup> The former authors have used both mass-spectrometry and effusion techniques and give the temperature dependence of the vapor pressure of the liquid as

$$a) \log_{10} p \text{ (atm)} = 5.59 \pm 0.07 - \frac{19950 \pm 90}{T}$$

(~1700° to 2050°K).

(IVA34-19)

For the sublimation of the solid, Karelin et al give

$$\log_{10} p \text{ (mm)} = 7.8130 - 15803/T \quad (1361^\circ \text{ to } 1761^\circ \text{K}),$$

or

(IVA34-20)

$$b) \log_{10} p \text{ (atm)} = 4.93 - 15803/T.$$

(IVA34-21)

which is seen to be quite at variance with the equation of Ackermann and Rauh. Although there is an overlap in the temperature range, Karelin et al made all their measurements below the melting point while Ackermann and Rauh straddled the melting point. The average heat of vaporization obtained from the equation of Ackermann and Rauh is  $91.3 \pm 0.4 \text{ kcal gfw}^{-1}$  and the weighted average of  $\Delta S^\circ$  is  $25.6 \pm 0.3 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}$ . The values derived from the data of Karelin et al are, respectively,  $72.31 \text{ kcal gfw}^{-1}$  and  $22.5 \text{ kcal gfw}^{-1}$ . In view of the extremely low value of  $\Delta H^\circ$  obtained by Karelin et al, it is believed that there is some error in their work; accordingly, the equation of Ackermann and Rauh is adopted here.

Using enthalpies from Jennings et al,<sup>16</sup> from Berg,<sup>4</sup> and from the monatomic gas table, by a "Second-Law" treatment,  $\Delta H_{298}^\circ (\text{sub}) = 98.7 \text{ kcal gfw}^{-1}$  and  $\Delta H_0 = 98.4 \text{ kcal gfw}^{-1}$  are obtained.

Alternatively,  $\Delta H_{298}^\circ$  is found, by a "Third-Law" calculation, as outlined below.

TABLE 20

THIRD-LAW CALCULATIONS OF  $\Delta H_{1298.15}^\circ$  OF  $\text{Y}_{(g)}$

T (°K)	$\log_{10} p^*$	$\Delta T^\circ \text{ (kcal gfw}^{-1})$	$-(\text{fef})_E$	$-(\text{fef})_s$	$-(\text{fef})$	$-T \Delta (\text{fef})$	$\Delta H_{1298.15}^\circ \text{ (kcal gfw}^{-1})$
1856	-5.16	43.82 <sub>1</sub>	48.49 <sub>5</sub>	17.58 <sub>0</sub>	30.91 <sub>5</sub>	57.37 <sub>8</sub>	101.20
1924	-4.78	42.08 <sub>1</sub>	48.65 <sub>6</sub>	17.89 <sub>1</sub>	30.76 <sub>5</sub>	59.19 <sub>2</sub>	101.27
1967	-4.56	41.04 <sub>4</sub>	48.75 <sub>8</sub>	18.08 <sub>2</sub>	30.67 <sub>6</sub>	60.34 <sub>0</sub>	101.38
2033	-4.22	39.25 <sub>8</sub>	48.89 <sub>9</sub>	18.37 <sub>0</sub>	30.52 <sub>9</sub>	62.06 <sub>6</sub>	101.32
2103	-3.90	37.52 <sub>9</sub>	49.06 <sub>4</sub>	18.66 <sub>8</sub>	30.39 <sub>6</sub>	63.92 <sub>3</sub>	101.45
Average							101.32 <sub>6</sub>

\*P is in atm.

By trial, it is found that  $\Delta F^\circ$  changes sign between 3600° and 3700°K and, by linear interpolation, is zero at 3604°K, which is the boiling point here adopted. The equation of Ackermann and Rauh<sup>21</sup> leads by direct extrapolation to a boiling point of 3570°K, and Brewer<sup>18</sup> had estimated 3500°K. The thermodynamic properties of yttrium in the reference table are included in this compilation.

#### 7) Thermodynamic functions of ideal monatomic gas

The heat of formation of yttrium ideal gas from the solid; i.e.,  $\Delta H_{\text{sub}}^\circ$  at 298.15°K, was estimated by Stull and Sinke<sup>10</sup> as 102 kcal gfw<sup>-1</sup>. The value here adopted is 101.326. The thermodynamic functions given in the ideal monatomic gas table were calculated from all the energy levels listed by Moore.<sup>23</sup>  $H_{298}^\circ - H_0^\circ$  was found to be 1638.91 cal gfw<sup>-1</sup> for the ideal gas. Calculations of this type have previously been performed by Kolsky, Gilmer, and Gilles.<sup>24</sup>

#### Supplement

DeMaria et al<sup>25</sup> have reported mass-spectrometric vaporization studies for yttrium.

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### 35. Zirconium

In an earlier report,<sup>1</sup> data used for compiling a zirconium reference table were discussed. Also, an incomplete ideal monatomic gas table was presented, the entries for  $\Delta H^\circ$ ,  $\Delta F^\circ$  and  $\log K_p^\circ$  being missing. The original report<sup>1</sup> accepted a heat of vaporization of 146 kcal gfw<sup>-1</sup>, based on the works of Skinner, Edwards, and Johnston,<sup>2</sup> and Stull and Sinke.<sup>3</sup> It was suggested by Leitnaker, Bowman, and Gilles<sup>4</sup> on the basis of vaporization studies for  $ZrB_2$  that the heat-of-sublimation value of zirconium might be too high. Accordingly, it seemed worthwhile to amend and possibly revise the reference and gas tables.

#### a. Reference Table

For the reference table, there did not appear to be any new data which would materially change the data previously used for the condensed phase portion of this table.

Heat-content data for zirconium had been reported by Fieldhouse and Lang<sup>5</sup> for the temperature range 391° to 2793°F (472° to 1807°K). At the highest temperature (1807°K), their data gave  $H_{T=H_{298}}^\circ$  12.162 kcal gfw<sup>-1</sup> which is only slightly smaller than the value of 12.313 kcal gfw<sup>-1</sup> interpolated from the earlier RAD tables.<sup>1</sup> In view of the good agreement, it appeared unnecessary to revise this portion of the tables.

Because of new vapor-pressure data to be discussed shortly, it was necessary to calculate a new boiling point and revise the reference table above the boiling point.

#### b. Monatomic Gas Table

The incomplete portion of the monatomic gas table shown in the earlier report<sup>1</sup> was retained.

A review of additional literature data on the sublimation of zirconium showed the following work. Fedorov<sup>6</sup> found a heat of sublimation of 49.0 kcal in the range 1100° to 1400°C. The data were obtained by a Second-Law method. Unfortunately, absolute pressures were not obtained, and hence Third-Law methods could not be used.

Additional work by Fedorov and Smirnov<sup>7</sup> for the temperature range 1267° to 1463°C gave a value of  $\Delta H_{\text{sublimation}}^\circ$  = 58.66 kcal gfw<sup>-1</sup>. These very low values found by Fedorov and Smirnov do not fit into the scheme of the periodic chart where heats of sublimation of titanium are 112 kcal, and for hafnium about 145 kcal. In private discussions, Fedorov<sup>8</sup> stated that he had repeated his experiments many times. Thus, a measurement error appears to be ruled out. It is possible that an impurity of

some type may have caused increased volatility. Thorn<sup>9</sup> pointed out that there was evidence that oxygen could cause increased volatility. Thus, for the present analysis, it seems that a serious error remains in this work as far as the heat of sublimation of zirconium is concerned.

Recently, new mass spectrometric measurements of the heat of sublimation of zirconium have been performed by Trulson and Goldstein.<sup>10</sup> From their data, they calculated a Third-Law heat of sublimation,  $\Delta H_{s298}^{\circ} = 140.9 \pm 3.1 \text{ kcal gfw}^{-1}$ .

For the present compilation, the original vapor-pressure data from Skinner et al,<sup>2</sup> and Trulson and Goldstein,<sup>10</sup> were recomputed, using free-energy functions from the present work. The results are shown below.

Reference	$\Delta H_{s298}^{\circ} \text{ (kcal gfw}^{-1}\text{)}$
Skinner <u>et al</u> <sup>2</sup>	145.412
Trulson and Goldstein <sup>10</sup>	140.840
Average	143.126

For this work, the average value for the heat of sublimation,  $\Delta H_{s298}^{\circ} = 143.126 \text{ kcal gfw}^{-1}$ , was accepted. This is subject to an estimated uncertainty of  $\pm 4 \text{ kcal}$ .

Using the above data, a new boiling point of 4644.05°K was computed. Finally, new reference and monatomic gas tables were compiled.

#### Supplement

Douglas<sup>11</sup> has reported high-temperature thermodynamic data for zirconium.

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## B. COMPOUNDS

### 1. Beryllium Compounds

The only beryllium compounds investigated in this study were the carbides, nitrides, and oxides.

#### 1.1 Beryllium Borides

The borides of beryllium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 1.2 Beryllium Carbides

In this study, detailed analyses of beryllium carbides were made for diberyllium carbide. In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

##### 1.2.1 Diberyllium Carbide ( $\text{Be}_2\text{C}_{(s,l)}$ )

###### a. Phase Data, Crystal Structure, and Melting Point

Beryllium carbide crystallizes in a face-centered-cubic (fcc), C1-type structure. The lattice parameter is 4.33 kX,<sup>1</sup> and no solid-state transformations have been reported.

This compound is reported by Oishi and Hamano<sup>2</sup> to decompose on heating to temperatures as low as 1873°K, while Brewer *et al.*,<sup>3</sup> and Gaev,<sup>4</sup> report melting or dissociation between 2373° and 2423°K. For the calculation of these tables, a melting temperature of 2400° ± 30°K is assumed, based upon the reported data. The heat of melting of 18.0 kcal gfw<sup>-1</sup> has been derived from the assumed melting point, and an assumed value of 2.5 cal gfw<sup>-1</sup> deg K<sup>-1</sup> as the entropy of melting. This value is accepted by NBS Report 6645,<sup>5</sup> and is based upon a survey of other "typical compounds."

###### b. Thermodynamic Properties

###### 1) Heat capacity

The heat capacity used in these tables is based upon the equation reported by Neely *et al.*<sup>6</sup> This has been extrapolated to the assumed melting point of 2400°K. Although the samples used in the determinations for these data are known to contain some oxide and nitride, no correction for these contaminants has been made. The heat-capacity equation used in the calculation of these tables is

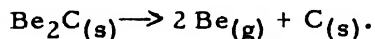
$$C_p^0 = 8.818 + 5.106 \times 10^{-3} T \quad \text{cal deg K}^{-1} \text{ gfw}^{-1}.$$

In the absence of heat-capacity data for the liquid state of beryllium carbide, the heat capacity of the liquid has been assumed to be equal to the solid at the melting point and constant up to 3500°K. The value of the liquid heat capacity assumed for the calculation of these tables is 21.072 cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

A 15-percent error has been assumed for the heat capacity of the solid over the range 298° to 2400°K, and for the liquid state an error of ± 3.0 cal gfw<sup>-1</sup>.

## 2) Standard heat of formation

The value for  $\Delta H_{f298}^0$  used for the calculations of these tables is  $-23.8 \pm 1.8$  kcal gfw<sup>-1</sup> and has been obtained by a Third-Law calculation of Pollock's vapor-pressure data for the reaction



This value agrees favorably with the value of  $-21.8 \pm 5$  kcal gfw<sup>-1</sup> Pollock<sup>7</sup> obtained by accepting Krikorian's<sup>8</sup> estimated value for the entropy. Krikorian estimated the  $\Delta H_{f298}^0$  to be  $-13.0 \pm 5$  kcal gfw<sup>-1</sup>. For NBS Report 6645,<sup>5</sup> a correction for the heat-capacity change in the decomposition reaction has been made; this has resulted in a value of  $-22.5 \pm 5$  kcal gfw<sup>-1</sup> based on Pollock's data. A Third-Law calculation of the vapor-pressure data reported by Baboin<sup>9</sup> gave a value of  $-39.8 \pm 2.8$  kcal gfw<sup>-1</sup>. A similar treatment of the vapor-pressure data reported in the Reactor Handbook<sup>10</sup> gave a low value of  $-4.97 \pm 0.25$  kcal gfw<sup>-1</sup>, and the vapor-pressure data of Muratov and Novoselova<sup>11</sup> resulted in a value of  $+10.6$  kcal gfw<sup>-1</sup>.

The vapor-pressure data used for these calculations are summarized in table 21.

## 3) Entropy

No low-temperature heat-capacity data have been reported for the compound, but Krikorian<sup>8</sup> estimated a value of  $-2.0 \pm 1.0$  per equivalent carbon which leads to  $S_{298}^0 = +4.0 \pm 1$  cal gfw<sup>-1</sup> deg K<sup>-1</sup>. This estimated value is used in the calculation of these tables.

TABLE 21

VAPOR-PRESSURE DATA USED FOR THIRD-LAW CALCULATION OF  
STANDARD HEAT OF FORMATION OF DIBERYLLIUM CARBIDE

Pollock <sup>7</sup>		Baboin <sup>9</sup>	
Temperature	P <sub>Be</sub>	Temperature	P <sub>Be</sub>
°K	atm	°K	atm
1430	$1.86 \times 10^{-7}$	1600	$6.57 \times 10^{-7}$
1434	$2.72 \times 10^{-7}$	1700	$2.89 \times 10^{-6}$
1442	$2.00 \times 10^{-7}$	1800	$1.03 \times 10^{-5}$
1446	$1.72 \times 10^{-7}$	1900	$3.81 \times 10^{-5}$
1515	$1.25 \times 10^{-6}$	2000	$1.09 \times 10^{-4}$
1536	$2.08 \times 10^{-6}$	2100	$8.81 \times 10^{-4}$
1578	$2.18 \times 10^{-6}$	2200	$2.24 \times 10^{-3}$
1580	$3.30 \times 10^{-6}$	2300	$5.26 \times 10^{-3}$
1590	$3.80 \times 10^{-6}$		
1628	$8.60 \times 10^{-6}$		
1643	$8.50 \times 10^{-6}$		
1647	$1.08 \times 10^{-5}$		
1659	$1.83 \times 10^{-5}$		
1660	$1.79 \times 10^{-5}$		

Reactor Handbook <sup>10</sup>		Muratov and Novoselova <sup>11</sup>	
Temperature	P <sub>Be</sub>	Temperature	P <sub>Be</sub>
°K	atm	°K	atm
1900	$6.0 \times 10^{-3}$	1673	$5.26 \times 10^{-3}$
2100	$4.0 \times 10^{-2}$	1716	$7.24 \times 10^{-3}$
2400	$4.4 \times 10^{-1}$	1773	$1.25 \times 10^{-2}$
2600	$1.5 \times 10^{-1}$	1837	$1.97 \times 10^{-2}$
		1873	$2.50 \times 10^{-2}$
		1953	$4.74 \times 10^{-2}$

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### 1.3 Beryllium Nitrides

In this study, detailed analyses of beryllium nitrides were made for  $\text{Be}_3\text{N}_2$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 1.3.1 Beryllium Nitride ( $\text{Be}_3\text{N}_2$ (s,l))

##### a. Phase Data, Crystal Structure, and Melting Temperature

Several investigators <sup>1, 2, 3</sup>, have determined the structure of beryllium nitride to be a b. c. c. lattice, with a D5 or anti- $\text{Mn}_2\text{O}_3$  structure. The lattice constant is  $8.13 \pm 0.10$  kX.

Eckerlin and Rabenau<sup>2</sup> report a phase transition at  $1400^\circ\text{C}$ . The new phase is hexagonal with  $a = 2.835$  and  $c = 9.673$  kX and they designate it  $\beta$ - $\text{Be}_3\text{N}_2$ . However, they report that small amounts of silicon or its compounds ( $\geq 0.1$  atom percent) accelerate the transformation and also that this accelerator need not be present for the transformation to occur. However, they also report that a reverse transformation to the cubic, alpha-phase has not been observed. They attribute this to an inhibited reaction. For these tables, the new phase was not considered because of the irreversibility of transformation and because of the possible presence of trace impurities.

The melting point of beryllium nitride is in question; it ranges from  $2273^4$  to  $2470^\circ\text{K}^5$  and for the calculations in these tables; a melting point of  $2470^\circ\text{K}$  was accepted.

##### b. Thermodynamic Functions

###### 1) Heat capacity

Sato<sup>6</sup> reports a heat capacity equation based upon measurements over the range 0 to  $500.3^\circ\text{C}$  ( $273$  to  $773.3^\circ\text{K}$ ), and Kelley<sup>7</sup> used these data to obtain a different relationship. For the calculation of these tables, the above data were treated by the Shomate<sup>8</sup> method. The new equation obtained is

$$C_p^\circ = 18.510 + 10.377 \times 10^{-3} T - 45.390 \times 10^{-4} T^2 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

No data are available for the liquid state, so the heat capacity was assumed to be equal to that of the solid at the assumed melting point of  $2470^\circ\text{K}$ . This yielded a value of  $44.06 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  which was assumed constant up to an arbitrary temperature of  $3500^\circ\text{K}$ .

The uncertainty in the heat capacity equation was obtained by comparing the values computed by the equation reported in NBS No. 6645<sup>9</sup> and the equation above. The discrepancy between these two equations was  $\pm 5$  percent up to 1500°K and  $\pm 8$  percent up to 2470°K. The error in the liquid heat capacity was assumed to be  $\pm 5.0$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

## 2) Heat of fusion

The heat of fusion, 30,875 cal gfw<sup>-1</sup>, was obtained by assuming an entropy of 2.5 cal °K<sup>-1</sup> g atom<sup>-1</sup> for the compound based upon a survey of "typical compounds" made in NBS Report No. 6645.<sup>9</sup> The uncertainty in this value was assumed to be  $\pm 3.7$  kcal gfw<sup>-1</sup> and was based upon a value of 3.0 cal °K<sup>-1</sup> g atom<sup>-1</sup> for the entropy.

## 3) Standard heat-of-formation

The standard heat of formation used in the calculation of these tables is  $\Delta H_{298.15}^\circ = -132 \pm 3$  kcal gfw<sup>-1</sup> and is obtained from NBS Report No. 6645.<sup>9</sup> It is derived from the work of Neumann *et al*<sup>10</sup> who nitrided 99.5 percent pure metal with a BeO catalyst at 980°C. Neumann *et al*<sup>11</sup> also obtained a value of -129 by combustion to the oxide. This value is not accepted because of the uncertainty in the value for BeO that was used in the calculation. Other values that are reported are -135.7, from NBS Report No. C500,<sup>12</sup> -133.6 from Brewer *et al*,<sup>5</sup> and -135 from Alpin *et al*.<sup>13</sup>

## 4) Entropy

No low-temperature heat capacity is available for this compound, but Kelley<sup>14</sup> estimated the entropy at 298.15°K to be  $12 \pm 2$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>. This value was used in the calculation of these tables.

## Supplement

Douglas and Payne<sup>15</sup> indicate that heat-content data for Be<sub>3</sub>N<sub>2</sub> have been obtained in the range 273° to 1173°K. These data are detailed in the work by Douglas and Beckett.<sup>16</sup>

Recent heat-of-formation data for Be<sub>3</sub>N<sub>2</sub> have been obtained by Gross<sup>17</sup> and by Greenbaum.<sup>18</sup> The heats of formation obtained are about -140 kcal/mole in these recent works.

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#### 1.4 Beryllium Oxides

In this study, detailed analyses of beryllium oxides were made for  $\text{BeO}_{(s,l)}$ ,  $\text{BeO}_{(g)}$ ,  $\text{Be}_2\text{O}_{2(g)}$ ,  $\text{Be}_3\text{O}_{3(g)}$ ,  $\text{Be}_4\text{O}_{4(g)}$ ,  $\text{Be}_5\text{O}_{5(g)}$ , and  $\text{Be}_6\text{O}_{6(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 3).

##### 1.4.1 Beryllium Oxides

$(\text{BeO}_{(s,l)}, \text{BeO}_{(g)}, \text{Be}_2\text{O}_{2(g)}, \text{Be}_3\text{O}_{3(g)}, \text{Be}_4\text{O}_{4(g)}, \text{Be}_5\text{O}_{5(g)}, \text{Be}_6\text{O}_{6(g)})$

Although thermodynamic tables for beryllium oxide and its polymers were available from the JANAF Thermochemical Panel compilation, new tables were prepared to reflect the changes introduced by the upgrading of the beryllium tables which was made possible by the emergence of the first experimental values of the element's heat of fusion and of the heat capacity of its liquid. Previously obtained thermodynamic functions for the ideal gas were retained.<sup>1</sup>

##### a. Formation of the Solid Phase

The standard heat of formation of  $\text{BeO}_{(s)}$  at 298.15°K reported by Cosgrove and Snyder,<sup>2</sup> -143.100 kcal/gfw, was adopted herein. An uncertainty of  $\pm 4.000$  kcal/gfw was assigned to it. This uncertainty, although considerably greater than the standard deviation given by the latter authors, reflects disparate results from two other, presumably equally reliable, sources (i.e., -145.3 kcal/gfw from Neumann, Kröger, and Kunz,<sup>3</sup> and -147.3 kcal/gfw from Roth, Börger, and Siemonsen<sup>4</sup>). Cosgrove and Snyder<sup>2</sup> tabulated results from other earlier measurements.

From emf measurements in the temperature range of 682° to 1040°C on the cell

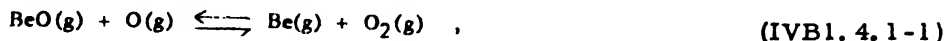


Smirnov and Chukreev<sup>5</sup> calculated the heat of formation of  $\text{BeO}_{(s)}$  to be -140.933 kcal/gfw.

##### b. Vaporization of Beryllium Oxide

The thermodynamic description of the vaporization of  $\text{BeO}$  was based on the mass spectrometric results of Chupka, Berkowitz, and Giese.<sup>6</sup> The latter authors determined the composition of the vapor above  $\text{BeO}_{(s)}$  in a tungsten Knudsen cell in the temperature range from 1900° to 2400°K. The principal vaporizing species were  $\text{Be}$ ,  $\text{O}$ ,  $\text{BeO}$ ,  $(\text{BeO})_n$ ,  $\text{O}_2$ ,  $\text{WO}_2$ ,  $\text{WO}_3$ , and  $\text{WO}_2(\text{BeO})_n$ . The trimer, tetramer, and pentamer were found to be the most important polymers of  $\text{BeO}$  under the conditions of the experiment.

The heat of formation of  $\text{BeO(g)}$  at  $298.15^\circ\text{K}$  was recalculated from equilibrium constants in the temperature range from  $2100^\circ$  to  $2474^\circ\text{K}$  given by Chupka, Berkowitz, and Giese<sup>6</sup> for the reaction



and thermodynamic functions for the appropriate species from the present compilation. The value of  $\Delta H_{f298}^\circ$  obtained for the gas was  $30.120 \pm 3.000$  kcal/gfw. The uncertainty estimate was based on a comparison of a calculated partial pressure of  $\text{BeO(g)}$  over  $\text{BeO(s)}$  at  $2242^\circ\text{K}$  with a partial pressure tabulated at that temperature by the authors cited.

Values for the heat of formation of  $\text{BeO(g)}$  could also be calculated from equilibrium constants for the reaction



given by the same authors cited above. However, as uncertainties in the ionization cross sections were more important for this reaction, data for reaction (IVB1. 4. 1-1) were preferred. The standard heat of formation for the gas of  $30.120$  kcal/gfw corresponds to a dissociation energy of  $106.4$  kcal/gfw. The best available value of the dissociation energy of  $\text{BeO(g)}$  is  $111$  kcal/gfw obtained by Lagerqvist<sup>7</sup> from spectroscopic data for the  $A^1\pi$  state of  $\text{BeO(g)}$  with the assumptions that this state dissociates to  $\text{Be}^1\text{S}$  and  $\text{O}^1\text{D}$ , and that the low-lying level of the singlet system is the ground state. The latter assumption appears valid because of the agreement with the thermochemical value of the dissociation energy. Also, Thrush<sup>8</sup> concluded that the low-lying  $^1\Sigma^+$  state of  $\text{BeO(g)}$  was the ground state from absorption spectra.

Chupka, Berkowitz, and Giese<sup>6</sup> also reported heats of vaporization at  $2150^\circ\text{K}$  for the  $\text{BeO}$  polymers (dimer through hexamer) derived from slopes of plots of the logarithm of ion-current times temperature versus reciprocal temperature. The calculations of the thermodynamic functions of the polymers given by Hildenbrand<sup>9</sup> were used to calculate the heats of formation of the polymers at  $298.15^\circ\text{K}$ , as well as the  $\Delta F_f^\circ$  and  $\log_{10} K_p$  values. These thermodynamic functions had been approximated by "assuming planar cyclic structures with Be-O distances of  $1.63\text{\AA}$  and crudely assigning one bending ( $600 \cdot \text{m}^{-1}$ ) and one stretching ( $1200 \text{ cm}^{-1}$ ) frequency for each Be-O bond, with additional estimated out-of-plane deformation frequencies where necessary."<sup>9</sup> From a combination of these thermodynamic functions, the uncorrected heats of vaporization of  $(\text{BeO})_n$  polymers at  $2150^\circ\text{K}$  given by Chupka, Berkowitz, and Giese,<sup>6</sup> and other appropriate thermodynamic functions from the present compilation, the following heats of formation for the ideal gases were calculated:

n	$\Delta H_{f298}^{\circ}(\text{kcal/gfw})$
2	$-101.700 \pm 16.000$
3	$-252.700 \pm 18.000$
4	$-377.600 \pm 24.000$
5	$-502.500 \pm 32.000$
6	$-632.800 \pm 40.000$

The uncertainties listed include only the sum of uncertainties in heats of vaporization at 2150°K as given by Chupka, Berkowitz, and Giese,<sup>6</sup> and those due to the uncertainty in the heat of formation of BeO(s) at 298.15°K as given here. They do not include an uncertainty estimate for the heat content of the appropriate (BeO)<sub>n</sub> gas.

A vaporization temperature of 4120°K was calculated with the assumption that vaporization by dissociation yielded Be(g) and O(g) (e. g., negligible O<sub>2</sub>(g) was produced) by determining at what temperature the sum of the partial pressures of all species equaled one atmosphere. The result was identical to the temperature estimated by Chupka, Berkowitz, and Giese,<sup>6</sup> although their prediction as to the vapor composition at that temperature differed from what follows from the thermodynamic functions given here. From the present calculations, dissociation to Be(g) and O(g) was accepted as the predominant reaction at 4120°K. Chupka, Berkowitz, and Giese<sup>6</sup> predicted that, at that temperature, the vapor would consist mostly of the tetramer with smaller amounts of the trimer and pentamer.

Other vaporization studies on BeO which did not include mass spectrometric determination of the vaporizing species were those of Erway and Seifert,<sup>10</sup> Pollock, Saul, and Milne,<sup>11</sup> Livey and Murray,<sup>12</sup> Belykh and Nesmeyanov,<sup>13</sup> and Firsova and Nesmeyanov.<sup>14, 15</sup> In the absence of partial pressure measurements, the most that could be concluded from these other studies was that the results were "consistent with" those of Chupka, Berkowitz, and Giese.<sup>6</sup> Douglas et al<sup>16</sup> and Ackermann and Thorn<sup>17</sup> found that the Chupka et al<sup>6</sup> data were consistent with the other data.

Amonenko et al<sup>18</sup> followed the vaporization of beryllium from a BeO crucible with a mass spectrometer. They reported that beryllium evaporated from solid Be primarily as the dimer and from liquid Be as the monomer. Above 1400°C, the reaction



was said to take place.  $\text{Be}_2\text{O}$  was reported to be more volatile than  $\text{BeO}$ . The former molecule might, therefore, be of importance in the vaporization of  $\text{BeO}$  under reducing conditions.

Young<sup>19</sup> had recently studied the reaction of  $\text{Be(s)}$  with  $\text{H}_2\text{O(g)}$ . Brewer and Trajmar<sup>20</sup> had reviewed the similarities between the electronic states of  $\text{C}_2$ ,  $\text{MgO}$ , and  $\text{BeO}$  and had recommended the use of the  $^3\pi$  ground states for high-temperature thermodynamic calculations on  $\text{BeO}$  and  $\text{MgO}$ . The use of the similarities in electronic states for the above-mentioned three molecules was suggested as a means of estimating energies of yet unobserved states.

#### Supplement

Victor and Douglas<sup>21</sup> have obtained thermodynamic properties of  $\text{BeO}$  from 298.15° to 1200°K.

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## 2. Boron Compounds

In this report, boron, carbon, nitrogen, and oxygen are normally considered to be nonmetallic elements, and therefore, such compounds as are formed by combining one of these nonmetallic elements with one of the 31 metallic elements are discussed under the appropriate metallic constituent in section IVB. Borides, carbides, nitrides, and oxides which could be found in the present category are discussed below.

### 2.1 Boron Borides

Semantically, the term "boron borides" has no correct meaning; however for the purposes of this report, this term is considered to denote elemental boron (section IVA2).

### 2.2 Boron Carbides

The carbides of boron were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 2.3 Boron Nitrides

The nitrides of boron were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 2.4 Boron Oxides

The oxides of boron were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 3. Calcium Compounds

The only calcium compounds investigated in this study were the oxides.

#### 3.1 Calcium Borides

The borides of calcium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 3.2 Calcium Carbides

The carbides of calcium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 3.3 Calcium Nitrides

The nitrides of calcium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 3.4 Calcium Oxides

In this study, detailed analyses of calcium oxides were made for  $\text{CaO}_{(s,l)}$  and  $\text{CaO}_{(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

### 3.4.1 Calcium Oxides ( $\text{CaO}_{(s,l)}$ , $\text{CaO}_{(g)}$ )

#### a. Condensed Phases

Values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  were calculated using  $\Delta H_{f298}^\circ = -151.410$  kcal/gfw\* for  $\text{CaO}(s)$  from the combustion results of Huber and Holley;<sup>1</sup> their paper contained a discussion of earlier determinations. An uncertainty of  $\pm 0.500$  kcal/gfw was assigned to this value of  $\Delta H_{f298}^\circ$ .

Previously reported<sup>2</sup> thermodynamic functions on  $\text{CaO}$  condensed phases were retained.

#### b. Gaseous Calcium Oxide

Thermodynamic functions for  $\text{CaO}(g)$  had been calculated on the basis of a  $^1\Sigma$  ground state and were reported in the first summary technical report.<sup>2</sup> They were recalculated with the assumption that the ground state is  $^3\Sigma$ .

As is also the case for  $\text{MgO}(g)$  and  $\text{SrO}(g)$ , dissociation energies determined from the known singlet system of  $\text{CaO}(g)$  are significantly lower than dissociation energies calculated from thermochemical data. In assuming that the discrepancy may be resolved by adopting a ground state as yet unobserved, the implicit assumptions have also been made that the Birge-Sponer extrapolation from the lowest singlet state to the lowest possible states of Ca and O is correct, and that polymeric molecules such as  $\text{Ca}_2\text{O}_2$  are not important.

Although the assumption of a triplet ground state is reasonable, the assumption that it is  $^3\Sigma$  is on less firm ground since it may be  $^3\Pi$  or  $^3\Delta$ . However, for the present compilation, a  $^3\Sigma$  ground state has been assumed for  $\text{MgO}(g)$ ,  $\text{CaO}(g)$ , and  $\text{SrO}(g)$ . It has also been assumed that the lowest  $^3\Sigma$  state is  $15000\text{ cm}^{-1}$  above the  $^1\Sigma$  ground state. This interval has been derived by decreasing the analogous interval of  $19200\text{ cm}^{-1}$  adopted for  $\text{MgO}(g)$ . A second  $^3\Sigma$  state at  $20000\text{ cm}^{-1}$  has also been assumed.

Spectroscopic constants for the triplet states were estimated. The spectroscopic constants used in the calculation were (in units of  $\text{cm}^{-1}$ ) as follows:

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\*The value  $-151.900$  kcal/gfw, given by Huber and Holley<sup>1</sup> was apparently based on an atomic weight of 40.18 for Ca.



TABLE 22

SPECTROSCOPIC CONSTANTS FOR CALCIUM OXIDE ( $\text{CaO(g)}$ )( $\text{cm}^{-1}$ )

State	E	$\omega_e$	$\omega_e x_e$	$B_e$	$a_e$	$D_e (\times 10^6)$
X $^3\Sigma$	( 0)	(850.0)	(5.0)	(0.53)	(0.004)	(0.7)
X' $^1\Sigma$	(15000)	732.11	4.81	0.44447	0.00335	0.656
$^3\Sigma$	(20000)	(725.0)	(4.0)	(0.45)	(0.003)	(0.7)
A $^1\Sigma$	26600	716.0	1.60	0.4063	0.00141	0.54
B $^1\pi$	40900	580.0	2.80	0.3882	0.0055	0.7
C $^1\Sigma$	43800	560.9	4.0	0.3731	0.0032	0.7

Spectroscopic constants between parentheses were estimated. Constants for the singlet states were those used previously,<sup>2</sup> with the exception of an addition of  $15000 \text{ cm}^{-1}$  to E.

A copious literature existed in which thermochemical data had been used to derive the dissociation energy of  $\text{CaO(g)}$ . None of the work could be regarded as definitive; however, most of it could be interpreted as showing that  $\text{CaO}$  vaporized primarily by dissociation to the gaseous elements. Past work had been reviewed by the following authors who selected the indicated dissociation energies at  $0^\circ\text{K}$ :

Source	$D_0^\circ$
	kcal/gfw
Brewer <sup>3</sup>	$103 \pm 8$
Brewer <sup>4</sup>	$90 \pm 12$
Gaydon <sup>5</sup>	$108 \pm 12$
Ackermann, Thorn, and Winslow <sup>6</sup>	99

A dissociation energy of 100 kcal/gfw was adopted herein. With this dissociation energy and appropriate thermodynamic functions for  $\text{CaO(g)}$ , O, and Ca from the present compilation,  $\Delta H_{f298}^\circ$  for  $\text{CaO(g)}$  was calculated to be 0.800 kcal/gfw. An uncertainty of  $\pm 15$  kcal/gfw was assigned to it.

A vaporization temperature, the temperature at which the sum of the partial pressures of all vaporizing species (excepting any polymeric species) equaled 1 atm, was calculated assuming the existence of equilibrium between O and  $\text{O}_2$ . The temperature so calculated was  $3890^\circ\text{K}$ . The partial pressure of undissociated  $\text{CaO(g)}$  at that temperature was 0.31 atm. An observed boiling point of  $3900^\circ\text{K}$  was reported by Mott.<sup>7</sup>

#### REFERENCES FOR SECTION IVB3.4.1

1. Huber, E. J. and C. E. Holley, J. Phys. Chem. 60, 498 (1956).
2. Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, Pt. I, Vol. 1, ASD TR 61-260 (May 1962).
3. Brewer, L., Chem. Revs. 52, 1 (1953).
4. Brewer, L., U.S. At. Energy Comm. Rept. UCRL-8356 (1958).
5. Gaydon, A. G., Dissociation Energies, 2nd ed., Chapman and Hall, London (1953).
6. Ackermann, R. J., R. J. Thorn, and G. H. Winslow, Planet. Space Sci. 3, 12 (1961).
7. Mott, W. R., Trans. Am. Electrochem. Soc. 34, 255 (1918).

#### 4. Carbon Compounds

In this report, boron, carbon, nitrogen, and oxygen are normally considered to be nonmetallic elements, and therefore, such compounds as are formed by combining one of these nonmetallic elements with one of the 31 metallic elements are discussed under the appropriate metallic constituent in section IVB. Borides, carbides, nitrides, and oxides which could be found in the present category are discussed below.

##### 4.1 Carbon Borides

The borides of carbon (more commonly called boron carbides) are referred to in section 2.2; however, as indicated there, no investigation was made.

##### 4.2 Carbon Carbides

Semantically, the term "carbon carbides" has no correct meaning; however for the purposes of this report, this term is considered to denote elemental carbon (section IVA4).

##### 4.3 Carbon Nitrides

The nitrides of carbon (e. g., cyanogen) were not investigated.

##### 4.4 Carbon Oxides

The oxides of carbon (e. g., carbon monoxide) were not investigated.

## 5. Cerium Compounds

The only cerium compounds investigated in this study were the oxides.

### 5.1 Cerium Borides

The borides of cerium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 5.2 Cerium Carbides

The carbides of cerium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 5.3 Cerium Nitrides

The nitrides of cerium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 5.4 Cerium Oxides

In this study, detailed analyses of cerium oxides were made for  $\text{CeO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 5. 4. 1 Cerium Monoxide ( $\text{CeO(g)}$ )

Vibrational constants used in the calculation of the thermodynamic functions of  $\text{CeO(g)}$  were taken from Herzberg.<sup>1</sup> In the absence of a rotational analysis, a value of  $B_e$  for the ground state was calculated from an estimated internuclear distance of 1.81Å. Values of  $B_e$  for higher electronic states were estimated from the assumption that the ratio  $\omega_e/B_e$  was constant for all electronic states.  $D_e$ 's were estimated from the relation  $D_e = 4B_e^3/\omega_e^2$ .

Herzberg<sup>1</sup> listed two systems of states for  $\text{CeO(g)}$  between which the intercombination energy was unknown. None of the states had been classified. It was assumed that each of the states listed by Herzberg had a multiplicity of 2, and that the state designated by him as (X') was 13700  $\text{cm}^{-1}$  above the state designated as (X) .

Spectroscopic constants used for the calculation of thermodynamic functions of  $\text{CeO(g)}$  were (in units of  $\text{cm}^{-1}$  where applicable) as follows:

TABLE 23

SPECTROSCOPIC CONSTANTS FOR CERIUM MONOXIDE ( $\text{CeO(g)}$ )( $\text{cm}^{-1}$ )

State	E	$\omega_e$	$\omega_e x_e$	$B_e$	$D_e (\times 10^7)$	$g^*$
(X)	0	865.0	2.99	(0.359)	(2.5)	(2)
A	12764.3	785.3	2.13	(0.326)	(2.2)	(2)
B	13817.2	788.3	1.76	(0.327)	(2.3)	(2)
(X')	(13720.0)	840.2	2.58	(0.349)	(2.3)	(2)
D	(34276.0)	791.7	1.72	(0.329)	(2.3)	(2)
E	(34584.0)	807.9	2.04	(0.335)	(2.3)	(2)

\*dimensionless.

Quantities in parentheses were estimated in whole or in part.

Walsh, Dever, and White<sup>2</sup> made a mass spectrometric study of the reaction



From this study of the reaction, it was reported that

$$\Delta H_{1870}^\circ = 1.05 \pm 0.20 \text{ kcal/gfw} \quad , \quad (\text{IVB5.4.1-2})$$

and

$$\Delta S_{1870}^\circ = 0.33 \pm 0.12 \text{ cal/}^\circ\text{K gfw} \quad . \quad (\text{IVB5.4.1-3})$$

Therefore, the difference between dissociation energies was

$$D_{1870}^{\circ}(\text{LaO}(\text{g})) - D_{1870}^{\circ}(\text{CeO}(\text{g})) = 1.05 \pm 0.20 \text{ kcal/gfw} \quad . \quad (\text{IVB5. 4. 1-4})$$

With the acceptance of the assumption of the latter authors that  $\Delta H_{1870}^{\circ} = \Delta H_0^{\circ}$ , then there resulted the relations

$$\begin{aligned} D_0^{\circ}(\text{CeO}(\text{g})) &= D_0^{\circ}(\text{LaO}(\text{g})) - (1.05 \pm 0.20) \\ &= (186.3 \pm 4.7) - (1.05 \pm 0.20) \\ &= 185 \pm 5 \text{ kcal/gfw} \quad . \quad (\text{IVB5. 4. 1-5}) \end{aligned}$$

$D_0^{\circ}$  for  $\text{LaO}(\text{g})$  was that given by Goldstein, Walsh, and White.<sup>3</sup> The value of  $\Delta H_{f298}^{\circ}$  for  $\text{CeO}(\text{g})$  calculated from this  $D_0^{\circ}$  was -31.100 kcal/gfw; an uncertainty of  $\pm 5.000$  kcal/gfw was assigned to it.

#### REFERENCES FOR SECTION IVB5. 4. 1

1. Herzberg, G., Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, 2nd ed., Van Nostrand, New York (1950).
2. Walsh, P. N., D. F. Dever, and D. White, J. Phys. Chem. 65, 1410 (1961).
3. Goldstein, H. W., P. N. Walsh, and D. White, J. Phys. Chem. 65, 1400 (1961).

## 6. Chromium Compounds

The only chromium compounds investigated in this study were the oxides.

### 6.1 Chromium Borides

The borides of chromium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 6.2 Chromium Carbides

The carbides of chromium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 6.3 Chromium Nitrides

The nitrides of chromium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 6.4 Chromium Oxides

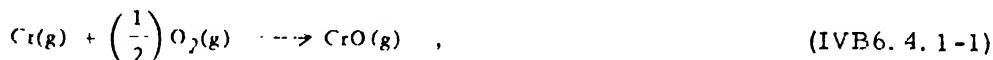
In this study, detailed analyses were made for  $\text{CrO}_{(g)}$ ,  $\text{CrO}_{2(s)}$ ,  $\text{CrO}_{2(g)}$ ,  $\text{CrO}_{3(s, l)}$  and  $\text{CrO}_{3(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 6.4.1 Chromium Monoxide ( $\text{CrO(g)}$ )

The physical properties of the condensed phases of  $\text{CrO}$  were not well known, and this oxide appeared to be of very minor importance as a solid oxidation product of chromium metal.<sup>1,2</sup> Consequently, no attempt was made to compile thermodynamic properties for the condensed phases of  $\text{CrO}$ . The existence of  $\text{CrO}$  in the gas phase at high temperatures had been verified by mass spectrographic studies.<sup>3</sup>

The spectroscopic constants (in  $\text{cm}^{-1}$  units) in table 24 employed in the calculation of thermodynamic functions for gaseous  $\text{CrO}$  are those given by Herzberg<sup>4</sup> (based on the work of Ghosh<sup>5</sup> and Ninomiya<sup>6</sup>).

The standard heat of formation of gaseous  $\text{CrO}$  at  $298.15^\circ\text{K}$ ,  $\Delta H_{f298}^\circ$ , had not been directly determined. It was therefore determined by an indirect method. Grimley, Burns, and Inghram,<sup>3</sup> in a mass spectrographic study of  $\text{Cr}_2\text{O}_3$ , measured the partial pressures of  $\text{CrO}$ ,  $\text{Cr}$ , and  $\text{O}_2$  in equilibrium at several temperatures in the range from  $1839^\circ$  to  $2059^\circ\text{K}$ . These measured pressures were used to obtain values for the equilibrium constant ( $K_p$ ) of reaction (IVB6.4.1-1)



$$K_p = \frac{P_{\text{CrO(g)}}}{P_{\text{Cr(l)}} P_{\text{O}_2}^{1/2}} \quad . \quad (\text{IVB6.4.1-2})$$

TABLE 24

THE SPECTROSCOPIC CONSTANTS OF GASEOUS  $\text{CrO}(\text{cm}^{-1})$

F	$\omega_e$	$\omega_e x_e$	$B_e$	$a_e$	$D_e (\times 10^7)$	$g^*$
0.0	898.8	6.5	0.5286	0.005	7.3	2.0
110.0	898.8	6.5	0.5286	0.005	7.3	2.0
220.0	898.8	6.5	0.5286	0.005	7.3	2.0
330.0	898.8	6.5	0.5286	0.005	7.3	2.0
440.0	898.8	6.5	0.5286	0.005	7.3	2.0
16520.0	750.7	8.9	0.475	0.0057	7.6	2.0
16620.0	750.7	8.9	0.475	0.0057	7.6	2.0
16720.0	750.7	8.9	0.475	0.0057	7.6	2.0
16820.0	750.7	8.9	0.475	0.0057	7.6	2.0
16920.0	750.7	8.9	0.475	0.0057	7.6	2.0

\*dimensionless.



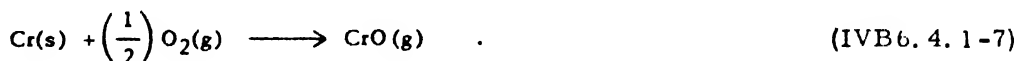
The standard free-energy change  $\Delta F^\circ$  for this reaction at the several temperatures was evaluated by means of equation (IVB6. 4. 1-3.)

$$\Delta F^\circ = -RT \ln K_p \quad . \quad (\text{IVB6. 4. 1-3})$$

The value of  $\Delta H_{298}^\circ$  for reaction (IVB6. 4. 1-1) was then obtained by means of equation (IVB6. 4. 1-4).

$$\frac{\Delta H_{298}^\circ}{T} = \frac{\Delta F^\circ}{T} + \Delta (f.e.f.) \quad . \quad (\text{IVB6. 4. 1-4})$$

The values of the free-energy functions for  $\text{CrO(g)}$ ,  $\text{Cr(g)}$ , and  $\text{O}_2(\text{g})$  were taken from the corresponding tables of this report and the summary technical report<sup>7</sup> on contract AF33(616)-7327.\*\* A value for  $\Delta H_{298}^\circ$  was calculated at each temperature for which Grimley and co-workers<sup>3</sup> reported measured pressures. The average of all the  $\Delta H_{298}^\circ$  values was combined with the  $\Delta H_{298}^\circ$  of sublimation of chromium to yield the heat of formation of gaseous  $\text{CrO}$  in accordance with the reaction scheme



The value of  $\Delta H_{f298}^\circ$  so obtained was  $+50,000 \pm 5,000$  cal/gfw. The value of  $H_{298}^\circ - H_0^\circ$  for  $\text{CrO}$  was calculated to be 2440 cal/gfw.

The tabulated values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  were then evaluated from the value of  $\Delta H_{f298}^\circ$  with equations (III E1-1) through (III E1-4).

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\*\*All these values can be found tabulated in volume 2 of this report.

#### REFERENCES FOR SECTION IVB6.4.1

1. Udy, M. J. , Chromium, Reinhold, N. Y. (1956).
2. Heslop, R. B. and P. L. Robinson, Inorganic Chemistry, Elsevier, Amsterdam (1960).
3. Grimley, R. T. , R. P. Burns, and M. G. Inghram, J. Chem. Phys. 34, 664 (1961).
4. Herzberg, G. , Molecular Spectra and Molecular Structure, I. Spectra of Diatomic Molecules, Van Nostrand, N. Y. (1950).
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7. Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, 2 Vols. ASD TR 61-260 Pt. I (May 1962).

#### 6. 4. 2 Chromium Dioxide ( $\text{CrO}_{2(s)}$ , $\text{CrO}_{2(g)}$ )

##### a. Solid State

Experimental data required for the calculation of the thermodynamic properties of solid  $\text{CrO}_2$  were virtually nonexistent. The tabulated thermodynamic properties reported herein were therefore largely based on estimated quantities.

##### 1) Entropy and heat capacity at 298.15°K

No experimental measurements of  $C_p^\circ$  appeared to have been made for solid  $\text{CrO}_2$ . However,  $C_{p298}^\circ$  and  $S_{298}^\circ$  data were available for the corresponding  $\text{MoO}_2$  and  $\text{WO}_2$  molecules.<sup>1, 2</sup> The values of  $S_{298}^\circ$  and  $C_{p298}^\circ$  for  $\text{CrO}_2$  were, therefore, estimated by the following scheme:

$$S_{298}^\circ(\text{MoO}_2) - S_{298}^\circ(\text{Mo}) = \Lambda, \quad (\text{IVB6. 4. 2-1})$$

$$S_{298}^\circ(\text{WO}_2) - S_{298}^\circ(\text{W}) = \Lambda', \quad (\text{IVB6. 4. 2-2})$$

$$S_{298}^\circ(\text{CrO}_2) - S_{298}^\circ(\text{Cr}) = \Lambda'', \quad (\text{IVB6. 4. 2-3})$$

The values of  $\Lambda$  and  $\Lambda'$  were calculated from the  $S_{298}^\circ$  values for  $\text{MoO}_2(s)$ ,  $\text{Mo}(s)$ ,  $\text{WO}_2(s)$ , and  $\text{W}(s)$ . A plot of  $\Lambda$  and  $\Lambda'$  versus the atomic number of the metallic element was then extrapolated to yield a value of  $\Lambda''$ . The value of  $\Lambda''$  was then used with the value of  $S_{298}^\circ$  for  $\text{Cr}(s)$  to calculate an estimated  $S_{298}^\circ$  value for  $\text{CrO}_2(s)$  of 9.90 e. u. from equation (IVB6. 4. 2-3). A corresponding procedure using heat capacities yielded an estimated  $C_{p298}^\circ$  of 13.38 cal/°K gfw for  $\text{CrO}_2(s)$ .  $H_{298}^\circ - H_0^\circ = 1900$  cal/gfw was estimated from a linear extrapolation of a plot of  $S_{298}^\circ$  versus  $H_{298}^\circ - H_0^\circ$  for the solid dioxides of W and Mo.

##### 2) Thermodynamic properties above 298.15°K

No thermodynamic properties of  $\text{CrO}_2(s)$  appeared to have been experimentally measured above room temperature. However,  $C_p^\circ$  data for the corresponding  $\text{MoO}_2$  and  $\text{WO}_2$  molecules had been determined and exhibited great similarity.<sup>2</sup> An estimated  $C_p^\circ$

equation for  $\text{CrO}_2(\text{s})$  was obtained by deriving an equation exhibiting approximately the same temperature dependence as the  $C_p^\circ$  equation for  $\text{MoO}_2(\text{s})$  and joining the estimated  $C_p^\circ$  298 value for  $\text{CrO}_2(\text{s})$ . The estimated equation thus obtained was (in  $\text{cal degK}^{-1} \text{gfw}^{-1}$ )

$$C_p^\circ = 14.13 + 5.80 \times 10^{-3}T - 2.20 \times 10^{-5}T^{-2} \quad (\text{IVB6. 4. 2-4})$$

Tabular values of  $C_p^\circ$  were calculated using this equation. Enthalpy, entropy, and free-energy values were then calculated from the related equations; i. e.,

$$H_T^\circ - H_{298}^\circ = 14.13T + 290 \times 10^{-5}T^2 + 2.20 \times 10^5T^{-1} - 5209 \quad (\text{cal gfw}^{-1}),$$

(IVB6. 4. 2-5)

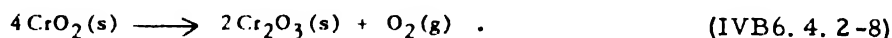
$$S_T^\circ = 14.13 \ln T + 5.80 \times 10^{-3}T + 1.10 \times 10^5T^{-2} - 73.573 \quad (\text{cal degK}^{-1} \text{gfw}^{-1}),$$

(IVB6. 4. 2-6)

$$- \left( \frac{H_T^\circ - H_{298}^\circ}{T} \right) = + S_T^\circ - \left( \frac{H_T^\circ - H_{298}^\circ}{T} \right) \quad (\text{cal degK}^{-1} \text{gfw}^{-1}).$$

(IVB6. 4. 2-7)

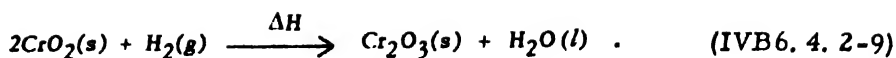
$\text{CrO}_2(\text{s})$  was reported not to exhibit a true melting or boiling point but to decompose to form  $\text{Cr}_2\text{O}_3$  and  $\text{O}_2$  according to equation (IVB6. 4. 2-8).



Brewer<sup>3</sup> has estimated that the oxygen pressure above  $\text{CrO}_2$  becomes 1 atm at 700°K, while the work of Kubota<sup>4</sup> has indicated that the reaction is essentially complete at temperatures slightly above 500°C. The condensed phase table presented herein was, therefore, extended only to 800°K.

### 3) Standard heat of formation at 298.15°K ( $\Delta H_f^\circ$ )

The only experimental determination of the standard heat of formation of  $\text{CrO}_2(\text{s})$  appeared to be that of Ariya and co-workers<sup>5</sup>. The latter workers measured the  $\Delta H$  of the reduction of  $\text{CrO}_2$  with  $\text{H}_2$  as in equation (IVB6. 4. 2-9).



This experimental  $\Delta H$  was then combined with the heat of formation of  $\text{H}_2\text{O}(\text{l})$  and of  $\text{Cr}_2\text{O}_3(\text{s})$  to yield the standard enthalpy of formation of  $\text{CrO}_2(\text{s})$ . The value of  $\Delta H_{f298}^\circ$  so obtained was  $-140.000 \pm 1.000$  kcal/gfw.

Tabulated values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  for  $\text{CrO}_2(\text{s})$  were then calculated using equations (III E1-1), (III E1-2), (III E1-3), and (III E1-4).

#### b. Gaseous State

No experimental spectroscopic data had been reported for gaseous chromium dioxide. All of the molecular constants required in the calculation of the thermodynamic functions of  $\text{CrO}_2$  were, therefore, estimated. The thermodynamic functions in the table for gaseous  $\text{CrO}_2$  were calculated with the molecular constants listed immediately below.

Molecular configuration:

Symmetric, nonlinear

$$\angle \text{O}-\text{Cr}-\text{O} = 107 \text{ degrees}$$

$$r_{\text{Cr}-\text{O}} = 1.627 \text{ \AA}$$

Product of moments of inertia:

$$I_A I_B I_C = 340637 \times 10^{-120} \text{ g}^3 \text{ cm}^6$$

Symmetry number:

$$\sigma = 2$$

Fundamental frequencies:

$$\omega_1 = 870 \text{ cm}^{-1}$$

$$\omega_2 = 388 \text{ cm}^{-1}$$

$$\omega_3 = 926 \text{ cm}^{-1}$$

Ground electronic state:

$$1\Sigma$$

The molecular configuration of  $\text{CrO}_2$  was unknown. Consideration of the periodic group to which chromium belongs and the work of Walsh<sup>6</sup> on bonding and structure relations leads to the conclusion that  $\text{CrO}_2$  is a symmetric nonlinear molecule, and it was so considered in the present work. As might be expected in the absence of experimental evidence, other workers may accept an alternative configuration. For example, the free-energy function for  $\text{CrO}_2$  at several selected temperatures was recently calculated by Grimley, Burns, and Inghram,<sup>7</sup> based on the assumption of Chandrasekharaiah and Brewer,<sup>8</sup> that the Group IV, V, and VI transition metal dioxides are all linear symmetric molecules. An  $\text{O}-\text{Cr}-\text{O}$  angle of 107 degrees was chosen in the present work as representing a reasonable value in comparison to known compounds of similar bonding. The  $\text{Cr}-\text{O}$  bond distance was assumed to be identical with the known distance for the chromium monoxide ( $\text{CrO}$ ) molecule; i. e., 1.627 Å.<sup>9</sup>

The moments of inertia of  $\text{CrO}_2$  were calculated using the above bond angles and bond distances with the following equations:<sup>10</sup>

$$I_x = \left( \frac{2M_O M_{\text{Cr}}}{2M_O + M_{\text{Cr}}} \right) r^2 \cos^2 a, \quad (\text{IVB6.4.2-10})$$

$$I_y = 2M_O r^2 \sin^2 a, \quad (\text{IVB6.4.2-11})$$

$$I_z = I_x + I_y, \quad (\text{IVB6.4.2-12})$$

$$I_A I_B I_C = I_x I_y I_z, \quad (\text{IVB6.4.2-13})$$

where  $M_O$  is the mass of the oxygen atom,  $M_{\text{Cr}}$  is the mass of the chromium atom,  $r$  is the  $\text{Cr}-\text{O}$  bond distance, and  $a$  is one-half of the  $\text{O}-\text{Cr}-\text{O}$  bond angle.

The estimation of the fundamental frequencies of  $\text{CrO}_2$  was carried out as explained in section IIIB3 of this report. The values of the fundamental frequencies ( $\omega_1$ ,  $\omega_2$ , and  $\omega_3$ ) were thus calculated from equations (IIIB3-2), (IIIB3-3), and (IIIB3-4) with estimated values of the bond-stretching and bending force constants.

The electronic states of  $\text{CrO}_2$  were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a  $^1\Sigma$  state was followed. This procedure is simpler and is believed to be as good as that used by other workers,<sup>8, 11</sup> who have estimated electronic levels from a crude ionic central-atom model.

The standard heat of formation of gaseous  $\text{CrO}_2$  at 298.15°K,  $\Delta H_{298}^\circ$ , had not been directly determined. It was therefore determined by an indirect method based on a mass spectrographic study of  $\text{Cr}_2\text{O}_3$  by Grimley, Burns, and Inghram.<sup>7</sup> The latter workers measured the partial pressures of  $\text{CrO}_2$ ,  $\text{Cr}$ , and  $\text{O}_2$  in equilibrium at several temperatures in the 1839° to 2059°K range. These measured pressures were used to obtain values for the equilibrium constant  $K_p$  of reaction (IVB6. 4. 2-14).



$$K_p = \frac{P_{\text{CrO}_2(\text{g})}}{P_{\text{Cr(g)}} P_{\text{O}_2(\text{g})}} \quad . \quad (\text{IVB6. 4. 2-15})$$

The standard free-energy change  $\Delta F^\circ$  for this reaction was evaluated by means of equation (IVB6. 4. 2-16)

$$\Delta F^\circ = -RT \ln K_p \quad . \quad (\text{IVB6. 4. 2. 16})$$

The  $\Delta H_{298}^\circ$  value for reaction (IVB6.4.2-14) was then obtained by means of equation (IVB6. 4. 2-17)

$$\frac{\Delta H_{298}^\circ}{T} = \frac{\Delta F^\circ}{T} + \Delta(\text{f.e.f.}) \quad . \quad (\text{IVB6. 4. 2-17})$$

The values of the free-energy functions for  $\text{CrO}_2(\text{g})$ ,  $\text{Cr(g)}$ , and  $\text{O}_2(\text{g})$  were taken from the compilations of this project. A value of  $\Delta H_{298}^\circ$  was calculated at each temperature for which Grimley and co-workers<sup>7</sup> reported measured pressures. The average of all the  $\Delta H_{298}^\circ$  values for the above reaction was then combined with the standard heat of

sublimation of chromium to yield the  $\Delta H_{f298}^\circ$  of gaseous  $\text{CrO}_2$  in accordance with the following reaction scheme:



The value of  $\Delta H_{f298}^\circ$  so obtained was  $-19.000 \pm 3.000$  kcal/gfw. The value of  $H_{298}^\circ - H_0^\circ$  for  $\text{CrO}_2$  was calculated to be 2640 cal/gfw.

The tabulated values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  were calculated from equations (IIIE1-1), (IIIE1-2), (IIIE1-3), and (IIIE1-4).

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### 6.4.3 Chromium Trioxide ( $\text{CrO}_3(\text{s}, \text{l}), \text{CrO}_3(\text{g})$ )

#### a. Condensed State

Insufficient experimental data were available for the exact calculation of the thermodynamic properties of condensed phase  $\text{CrO}_3$ . The thermodynamic functions of  $\text{CrO}_3$  given herein were, therefore, primarily based on estimated quantities.<sup>1-12</sup>

##### 1) Entropy and heat capacity at 298.15°K

No experimental measurements of  $C_p^\circ$  appeared to have been made for solid  $\text{CrO}_3$ . However,  $C_p^\circ$  and  $S_{298}^\circ$  data were available for the corresponding  $\text{MoO}_3$  and  $\text{WO}_3$  molecules.<sup>8</sup> The values of  $S_{298}^\circ$  and  $C_p^\circ$ , as estimated by a procedure corresponding to that employed for  $\text{CrO}_2(\text{s})$ , were 18.26 e. u. and 18.09 cal/°K gfw.  $H_{298}^\circ - H_0^\circ = 2970$  cal/gfw was estimated from a linear interpolation of a plot of  $S_{298}^\circ$  versus  $H_{298}^\circ - H_0^\circ$  for solid trioxides of W and Mo.

##### 2) Melting point and heat of fusion

Values ranging from 453° to 471°K have been quoted or reported<sup>1-4</sup> for the melting point of  $\text{CrO}_3$ . A value of 470° ± 10°K was chosen as the most probable melting point.

The heat of fusion of  $\text{CrO}_3$  was unknown. A value of 5358 cal/gfw was estimated from an assumed  $\Delta S$  of fusion of 11.40 e. u. at the melting point. The assumed  $\Delta S$  of fusion was selected by comparison with the known values for the corresponding  $\text{MoO}_3$  and  $\text{WO}_3$  molecules.

##### 3) Thermodynamic functions for the condensed state

No heat-capacity measurements on solid  $\text{CrO}_3$  had been reported. However,  $C_p^\circ$  data for the corresponding  $\text{MoO}_3$  and  $\text{WO}_3$  molecules had been determined and exhibited marked similarity.<sup>8</sup> An estimated  $C_p^\circ$  equation for  $\text{CrO}_3(\text{s})$  was derived in a manner to that used in the case of  $\text{CrO}_2(\text{s})$ . The heat capacity, enthalpy, entropy, and free-energy equations so derived for  $\text{CrO}_3(\text{s})$  were

$$C_p^\circ = 18.12 + 7.80 \times 10^{-3}T - 2.10 \times 10^{-5}T^2 \quad \text{cal degK}^{-1} \text{gfw}^{-1}, \quad (\text{IVB6. 4. 3-1})$$

$$H_T^\circ - H_{298}^\circ = 18.12T + 390 \times 10^{-5}T^2 + 2.10 \times 10^{-5}T^3 - 6453 \quad \text{cal gfw}^{-1}, \quad (\text{IVB6. 4. 3-2})$$

$$S_T^\circ = 18.12 \ln T + 7.80 \times 10^{-3}T + 1.05 \times 10^5 T^{-2} - 88.488 \quad \text{cal degK}^{-1} \text{gfw}^{-1},$$

(IVB6. 4. 3-3)

$$- \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) + S_T^\circ - \left( \frac{H_T^\circ - H_{298}^\circ}{T} \right) \quad \text{cal degK}^{-1} \text{gfw}^{-1}.$$

(IVB6. 4. 3-4)

The  $C_p^\circ$  of liquid  $\text{CrO}_3$  was estimated to be 29.00 cal/°K gfw by the rule given by Kubaschewski and Evans<sup>5</sup>, (i. e., the heat capacity of a liquid compound is approximately 7.25 times the number of atoms in the compound). The corresponding equations for the enthalpy, entropy, and free energy of liquid  $\text{CrO}_3$  were, therefore, (IVB6. 4. 3-4), (IVB6. 4. 3-5), and (IVB6. 4. 3-6).

$$H_T^\circ - H_{298}^\circ = 29.00T - 4900 \quad \text{cal gfw}^{-1},$$

(IVB6. 4. 3-5)

$$S_T^\circ = 29.00 \ln T - 139.888 \quad \text{cal degK}^{-1} \text{gfw}^{-1}.$$

(IVB6. 4. 3-6)

$\text{CrO}_3$  was found not to exhibit a true boiling point and to decompose with evolution of  $\text{O}_2$ . Intermediate chromium oxides are formed during the decomposition, and the end chromium oxide appears to be  $\text{Cr}_2\text{O}_3$ .<sup>2, 6, 7</sup> The decomposition is apparently essentially complete in the range of 700° to 800°K.

#### 4) Standard heat of formation at 298.15°K ( $\Delta H_{f298}^\circ$ )

The work of Roth and Becker,<sup>8</sup> Roth and Wolf,<sup>9</sup> Muldrow and Hepler,<sup>10</sup> and Neugebauer and Margrave<sup>11</sup> could be used to determine  $\Delta H_{f298}^\circ$  for  $\text{CrO}_3(\text{s})$ . An average value of  $-141.400 \pm 2.500$  kcal/gfw was thus obtained. Mah's<sup>12</sup> value of  $\Delta H_{f298}^\circ$  for  $\text{Cr}_2\text{O}_3(\text{s})$  was used in these calculations.

Tabulated values for  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  were calculated from equations (IIIE1-1), (IIIE1-2), (IIIE1-3), and (IIIE1-4).

#### b. Gaseous State

No experimental spectroscopic data had been reported for gaseous chromium trioxide. All of the molecular constants required for the calculation of the thermodynamic functions in the table for gaseous  $\text{CrO}_3$  were, therefore, estimated to be as follows:

Molecular configuration:

Planar, symmetric, cart wheel

$$\angle \text{O-Cr-O} = 120 \text{ degrees}$$

$$r_{\text{Cr-O}} = 1.627 \text{ \AA}$$

Product of moments of inertia:

$$I_A I_B I_C = 2346881 \times 10^{-120} \text{ g}^3 \text{ cm}^6.$$

Symmetry number:

$$\theta = 6.$$

Fundamental frequencies:

$$\omega_1 = 840 \text{ cm}^{-1}$$

$$\omega_2 = 397 \text{ cm}^{-1}$$

$$\omega_3 = 1023 \text{ cm}^{-1} (\text{Multiplicity} = 2)$$

$$\omega_4 = 347 \text{ cm}^{-1} (\text{Multiplicity} = 2)$$

Ground electronic state:

$$1_{\Sigma}$$

The molecular configuration of  $\text{CrO}_3$  was unknown. The molecule was assumed to be a symmetrical, planar cart-wheel. The only reasonable alternative structure was pyramidal; however, the pyramidal structure was considered to be unlikely in view of the known planar structure of other molecules having central atoms in the same periodic group as chromium; e. g.,  $\text{SO}_3$ . The Cr-O bond distance was assumed to be identical with the known corresponding distance for the chromium monoxide ( $\text{CrO}$ ) molecule; i. e.,  $1.627 \text{ \AA}$ .<sup>13</sup>

The moments of inertia of  $\text{CrO}_3$  were calculated for the assumed structure using the following equations:<sup>14</sup>

$$I_x = I_y = \frac{3M_{\text{O}} r^2}{2}, \quad (\text{IVB6. 4. 3-7})$$

$$I_z = I_x + I_y \quad , \quad (\text{IVB6. 4. 3-8})$$

$$I_A I_B I_C = I_x I_y I_z \quad , \quad (\text{IVB6. 4. 3-9})$$

where  $M_O$  is the mass of oxygen atom, and  $r$  is the Cr-O bond distance.

The estimation of the fundamental frequencies of  $\text{CrO}_3$  was based on the following assumptions:

- 1) The fundamental vibrations could be described by a valence force field method.<sup>15</sup>
- 2) The stretching force constant ( $k_1$ ) for  $\text{CrO}_3$  was calculated from an estimated value for the corresponding frequency  $\omega_1$  by means of equation (IVB6. 4. 3-10),

$$k_1 = 0.3548 \times 10^{23} M_O \omega_1^2 \quad . \quad (\text{IVB6. 4. 3-10})$$

The value of  $\omega_1$  was estimated by considering the  $\text{CrO}_3$  molecule to be approximately a  $\text{CrO}_2$  molecule ( $\angle \text{O-Cr-O} = 120$  degrees) with an additional O atom attached and calculating a value of  $\omega_1$  corresponding to this pseudo-molecule (i.e.,  $\omega_1^*$ ) by the procedure described in the section on the  $\text{CrO}_2$  molecule. The value  $847 \text{ cm}^{-1}$  was thus obtained for  $\omega_1^*$ . This value was then arbitrarily lowered to take into account the additional mass of the third oxygen atom. The value thus chosen for  $\omega_1^*$  was  $840 \text{ cm}^{-1}$ .

- 3) The other force constants ( $k_\lambda$  and  $k_\delta$ ) were calculated as explained in section IIIB4.

The values of the fundamental frequencies were then calculated from equations (IIIB4-3) through (IIIB4-6).

The electronic states of  $\text{CrO}_3$  were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a  $^1\Sigma$  state was followed.

The determination of the standard heat of formation of gaseous  $\text{CrO}_3$  was based on the mass spectrographic data of Grimley, Burns, and Inghram.<sup>16</sup> The latter workers had reported the partial pressures of  $\text{CrO}_3$ ,  $\text{Cr}$ , and  $\text{O}_2$  in equilibrium at  $1890^\circ$ ,  $1911^\circ$ , and  $1942^\circ\text{K}$ . These measured pressures were used to obtain the equilibrium constant ( $K_p$ ) and standard

free-energy ( $\Delta F^\circ$ ) value for reaction (IVB6. 4. 3-11) by means of equations (IVB6. 4. 3-12) and (IVB6. 4. 3-13).



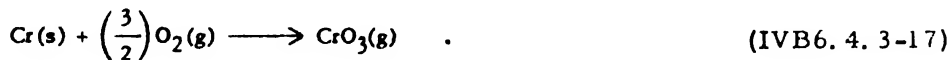
$$K_p = \frac{P_{\text{CrO}_3\text{(g)}}}{P_{\text{Cr(g)}} P_{\text{O}_2\text{(g)}}^{3/2}} \quad , \quad (\text{IVB6. 4. 3-12})$$

$$\Delta F^\circ = -RT \ln K_p \quad . \quad (\text{IVB6. 4. 3-13})$$

$\Delta H_{298}^\circ$  values for reaction (IVB6. 4. 3-11) were then calculated from equation (IVB6. 4. 3-14)

$$\frac{\Delta H_{298}^\circ}{T} = \frac{\Delta F^\circ}{T} + \Delta(f.e.f.) \quad . \quad (\text{IVB6. 4. 3-14})$$

The values of the free-energy functions for  $\text{CrO}_3\text{(g)}$  ,  $\text{Cr(g)}$  , and  $\text{O}_2\text{(g)}$  were taken from the corresponding tables of this project. The average value of  $\Delta H_{298}^\circ$  so obtained for reaction (IVB6. 4. 3-11) was then used with the standard heat of sublimation of chromium metal at 298.15°K to yield the  $\Delta H_{f298}^\circ$  of gaseous  $\text{CrO}_3$  by means of Hess's law.



The value of  $\Delta H_{f298}^\circ$  was thus calculated to be  $-68.400 \pm 3.000$  kcal/gfw. The value of  $H_{298}^\circ - H_0^\circ$  for  $\text{CrO}_3\text{(g)}$  was calculated to be 3108 cal/gfw.

The values of  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  were calculated in the usual manner from equations (IIIE1-1), (IIIE1-2), (IIIE1-3), and (IIIE1-4).

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## 7. Dysprosium Compounds

Detailed analyses were not made for these compounds.

### 7.1 Dysprosium Borides

The borides of dysprosium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 7.2 Dysprosium Carbides

The carbides of dysprosium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 7.3 Dysprosium Nitrides

The nitrides of dysprosium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 7.4 Dysprosium Oxides

The oxides of dysprosium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

## 8. Gadolinium Compounds

Detailed analyses were not made for these compounds.

### 8.1 Gadolinium Borides

The borides of gadolinium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2 ).

### 8.2 Gadolinium Carbides

The carbides of gadolinium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2 ).

### 8.3 Gadolinium Nitrides

The nitrides of gadolinium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2 ).

### 8.4 Gadolinium Oxides

The oxides of gadolinium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2 ).



## 9. Hafnium Compounds

Selected borides, carbides, nitrides, and oxides of hafnium were investigated.

### 9.1 Hafnium Borides

A detailed analysis is presented for hafnium diboride. In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 9.1.1 Hafnium Diboride ( $\text{HfB}_{2(s,l)}$ )

Reviews of data for various borides including the Hf-B system have been given by Samsonov and Markovskii,<sup>1</sup> Aronsson,<sup>2</sup> Hansen and Anderko,<sup>3</sup> Aronsson,<sup>4</sup> Steinitz,<sup>5</sup> and Schwarzkopf and Kieffer.<sup>6</sup>

##### a. Phase Data, Crystal Structure, and Melting Point

In their book, Hansen and Anderko<sup>3</sup> did not have sufficient information to give a phase diagram for the hafnium-boron system. Glaser, Moskowitz, and Post<sup>7</sup> prepared specimens of  $\text{HfB}_2$  by hot pressing at 2000°C. The specimens were isomorphous with  $\text{ZrB}_2$  having a hexagonal structure with  $a = 3.141 \pm 0.002 \text{ \AA}$  and  $c = 3.470 \pm 0.002 \text{ \AA}$ . They determined a melting point of 3523°K (3250° ± 100°C) with an optical pyrometer. For preparations containing less than 66.7-atom-percent B, they detected an fcc phase considered to be HfB. They also attempted to prepare  $\text{HfB}_{12}$  but could not.

More recently, Rudy and Benesovsky<sup>8</sup> reported that HfB of the B1-type structure (fcc) could not be obtained in pure preparations. However, they did report an HfB phase of the B27 type (FeB type) with lattice constants,  $a = 6.517 \text{ \AA}$ ,  $b = 3.219 \text{ \AA}$ , and  $c = 4.919 \text{ \AA}$ . Nowotny, Rudy, and Benesovsky,<sup>9</sup> from studies of the Hf-B-C ternary at 1400° and 1500°C, also reported that the monoboride with FeB structure is a stable phase. Recent communications by Nowotny,<sup>10,11</sup> and Aronsson<sup>12</sup> confirm that the monoboride of the FeB type is probably a stable phase, whereas the cubic monoboride is not.

Thus, it appears that the two most important phases in the Hf-B system are the monoboride and diboride. By analogy with the Zr-B and Ti-B system, it is to be expected that the diboride is much more refractory. Since more data are also available for the diboride, preparation of thermodynamic tables will be restricted to this phase.

Aronsson<sup>4</sup> indicates that  $\text{HfB}_2$  is a nonstoichiometric compound with a narrow range of homogeneity because no significant change of lattice parameters occurs with change in composition. This is to be expected since  $\text{TiB}_2$  and  $\text{ZrB}_2$  also exhibit narrow ranges of homogeneity. Aronsson<sup>4</sup> also lists the lattice parameters and melting point of 3250°C already mentioned as having been found by Glaser et al.<sup>7</sup> Earlier, Moers<sup>13</sup> had reported a melting point of 3100°C (3373°K). Post, Glaser, and Moskowitz<sup>14</sup> list the melting point as 3240°C (3513°K). For the present work, the melting point of 3250°C (3523°K) reported by Glaser et al.<sup>7</sup> is accepted.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

At the present time, there are no experimental determinations of the heat capacity at low temperature for  $\text{HfB}_2$ . However in the near future, it is expected that Westrum will complete such measurements.<sup>15</sup> (See Supplement for latest work.)

Estimates of the entropy at 298.15°K have been made here in section IIID8 by use of the Lindemann equation to estimate Debye temperatures. It has been found that  $C_{p,298.15}^\circ = 10.290 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 11.068 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , and  $H_{298.15}^\circ - H_0^\circ = 1.706 \text{ kcal gfw}^{-1}$ . Kaufman and Clougherty<sup>16</sup> estimated  $S_{298.15}^\circ = 9.69 \text{ e. u.}$ , and Mezaki et al<sup>17</sup> used the Latimer technique to give  $S_{298.15}^\circ = 11.2 \text{ e. u.}$

For the present calculation, the value of  $S_{298.15}^\circ = 11.068 \text{ e. u.}$  estimated here has been utilized. This value is in reasonable agreement with the other estimates. The accepted value of  $C_{p,298.15}^\circ$  has been rounded off to a value of  $12.000 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  to give a value intermediate between the estimated value of  $10.290 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  and the value of  $14.23 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  derived by Mezaki et al<sup>17</sup> from high-temperature heat-content measurements. In arriving at the choice of  $C_{p,298.15}^\circ$ , comparisons have also been made with the data of  $\text{ZrB}_2$  and  $\text{TiB}_2$  accepted in this work. The values accepted for  $C_{p,298.15}^\circ$  and  $S_{298.15}^\circ$  are still considered subject to a moderately large uncertainty.

### 2) High-temperature heat content

Mezaki et al<sup>17</sup> have made heat-content measurements in the range of 486.3° to 1149.9°K using a copper-block, drop-type calorimeter. Their raw data and smoothed data at 1200°K have both been reported. Pears et al<sup>18</sup> have reported enthalpy data for a wider temperature range of 599.8° to 2813.7°K (620° to 4605°F). Their original data in English units and data converted to cgs units are shown in table 25.

For the purpose of deriving a heat-capacity equation, the Shomate method was used. Both the enthalpy data from Mezaki et al<sup>17</sup> and Pears et al<sup>18</sup> were used.

The Pears et al<sup>18</sup> data have not been corrected by the small correction (probably  $-300 \text{ cal gfw}^{-1}$ ) to give an  $H_T^\circ - H_{298.15}^\circ$  value. Because of the fact that the value  $C_{p,298.15}^\circ = 12.000 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  is expected to be relatively inaccurate, the resulting equation is not expected to be precise. Furthermore, it is anticipated that low-temperature, experimental heat-capacity data will be available fairly soon which will make possible a better equation. From the present analysis, the equation derived is

$$C_p^\circ = 17.632 + 1.867 \times 10^{-3}T - 5.501 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

TABLE 25

HEAT-CONTENT DATA FROM PEARS et al<sup>18</sup>  
AS REPORTED AND CONVERTED TO cgs UNITS

Temperature $t$	Temperature $T$	$H_t^\circ - H_{32^\circ F}^\circ$	$H_T^\circ - H_{273.15^\circ K}^\circ$
$^\circ F$	$^\circ K$	Btu/lb	cal/gfw
620	599.8	43.5	4836.71
671	628.2	51.3	5703.99
1252	950.9	99.5	11063.29
2090	1416.5	168.0	18679.72
2550	1672.0	234.0	26018.18
2955	1897.0	263.0	29242.65
3485	2191.5	333.0	37025.87
3500	2199.8	323.0	35913.98
4000	2477.6	374.0	41584.61
4260	2622.0	401.0	44586.71
4600	2810.9	465.0	51702.79
4605	2813.7	460.0	51146.85

This equation valid for 298.15° to 2813°K has been extrapolated to the melting point at 3523°K. The value of the liquid heat capacity at this temperature is considered equal to the solid heat capacity at this and higher temperatures. The heat of fusion is estimated to be 20.0 kcal/gfw.

### 3) Heat of formation

Krikorian<sup>19</sup> has estimated the heat of formation for HfB to be -48.0 kcal/mole but gives no estimate for HfB<sub>2</sub>. Kaufman and Clougherty<sup>16</sup> have estimated the heat of formation to be -69.0 kcal/mole. Paderno, Serebryakova, and Samsonov<sup>20</sup> have used a tensimetric

method to derive a heat of formation of -74.2 kcal/mole. They have studied the reaction of hafnium dioxide with boron carbide and boron in the temperature range of 800° to 1800°C. In their tensimetric method, they usually observe the rate of change of pressure of the gaseous component (e. g., carbon monoxide). A rapid rate of change is considered to indicate the start of a new reaction. In the present case, Paderno *et al*<sup>20</sup> give practically no details, and hence it is not possible to evaluate their data. In general, the tensimetric method does not appear to achieve equilibrium conditions and may yield incorrect results. The value of the heat of formation found, however, appears reasonable when compared to the values already accepted herein for  $\text{TiB}_2$  and  $\text{ZrB}_2$ ; i. e.,  $\Delta H_{f298.15}^\circ = -66.850$  and  $-73.0$  kcal/mole, respectively. It is to be expected that the heat of formation for  $\text{HfB}_2$  being a related compound with a higher atomic number might be slightly more negative.

Rudy and Benesovsky<sup>8</sup> (p. 427) indicate that from a study of the reaction  $\text{HfB}_2 + 3/2 \text{N}_2 \rightarrow \text{HfN} + 2\text{BN}$  that the free energy of formation of  $\text{HfB}_2$  at 1400°C < -80 kcal/mole.

A fairly comprehensive study of the vaporization of hafnium diboride has been made by Krupka.<sup>21</sup> He used a tungsten effusion cell over the temperature range of 2175° to 2500°K. Some of the experiments have been conducted in an ultra-high-vacuum apparatus to produce vacuums of  $1 \times 10^{-12}$  atm or better.

He found that the diboride phase vaporizes congruently at  $\text{HfB}_{1.955 \pm 0.010}$  for temperatures to 2730°K. He considered the reaction of vaporization to be  $\text{HfB}_{1.955(s)} \rightarrow \text{Hf}_{(g)} + 1.955 \text{B}_{(g)}$ .

The original vapor-pressure data obtained by Krupka<sup>21</sup> have been recalculated using free-energy functions for  $\text{Hf}_{(g)}$  and  $\text{B}_{(g)}$  from the present work. Free-energy functions from the present tabulation for  $\text{HfB}_2$  have been converted to free-energy functions for  $\text{HfB}_{1.955}$

by multiplying by the factor  $\frac{2.955}{3.000} = 0.985$ . Krupka<sup>21</sup> has in-

dicated that, because of their lower mass, B atoms will diffuse more rapidly out of the effusion cell. Hence, the partial pressure of  $\text{B}_{(g)}$  is lower in the Knudsen cell than would be expected under ideal equilibrium conditions. Krupka<sup>21</sup> (p. 78) shows that

$$P_B = P_{\text{Hf}} \times 1.955 \sqrt{\frac{n_{\text{mole wt B}}}{n_{\text{mole wt Hf}}}} \text{ or } P_B = 0.4813 P_{\text{Hf}} .$$

Using Krupka's values for  $P_{\text{Hf}}$  and calculating  $P_{\text{B}}$  values as indicated above, calculations have been made of the heat of decomposition  $\Delta H_{298.15}^\circ$  for the reaction,  $\text{HfB}_{1.955}(\text{s}) \rightarrow \text{Hf}(\text{g}) + 1.955 \text{ B}(\text{g})$ . The results are shown in table 26.

TABLE 26

SUMMARY OF RECALCULATION OF KRUPKA<sup>21</sup> DATA FOR REACTION  
 $\text{HfB}_{1.955}(\text{s}) \rightarrow \text{Hf}(\text{g}) + 1.955 \text{ B}(\text{g})$

Case	Krupka Page Reference and Type of Data	Series	$\Delta H_{298.15}^\circ$ (via Krupka)	$\Delta H_{298}^\circ$ (present calculations)
	Page    Type		cal/mole	cal/mole
2	88 -- weight loss; ultra-high vacuum	WL	481,115	488,968.7
3	90 -- high vacuum	B	482,134	490,126.6
4	92 -- high vacuum	C	485,043	493,030.2
5	95 -- high vacuum	D	479,467	487,451.9
6	97 -- high vacuum	F	479,006	487,005.3
7	100 -- ultra-high vacuum	H	482,210	489,114.0
Average of Cases 2 to 7				489,282.7

For  $\text{HfB}_{1.955}(\text{s}) \rightarrow \text{Hf}(\text{g}) + 1.955 \text{ B}(\text{g})$

$$\Delta H_{298.15}^\circ = \Delta H_{\text{fHf}(\text{g})}^\circ + 1.955 \Delta H_{\text{fB}(\text{g})}^\circ - \Delta H_{\text{fHfB}_{1.955}}^\circ \quad \text{or}$$

$$\begin{aligned} \Delta H_{\text{fHfB}_{1.955}}^\circ, 298.15 &= \Delta H_{\text{fHf}(\text{g})}^\circ + 1.955 \Delta H_{\text{fB}(\text{g})}^\circ - \Delta H_{298.15}^\circ \\ &= 144.924 + 1.955 \times 133.0 - 489.282, \end{aligned}$$

$$\Delta H_{\text{fHfB}_{1.955}}^\circ, 298.15 = -84.343 \text{ kcal/mole.}$$

Thus, from the vaporization data of Krupka,<sup>21</sup> a heat of formation of  $\text{HfB}_{1.955}$ ,  $\Delta H_{f298.15}^\circ = -84.343$  kcal/mole is derived. If it is assumed that the value for the stoichiometric compound is proportional to the number of molecules,

$$\Delta H_{f298.15}^\circ, \text{HfB}_2 = \frac{3}{2.955} \times (-84.343) = -85.627 \text{ kcal/mole}$$

is obtained.

In making the above calculation, it is seen that several sources of errors can arise, including not only errors in the original vapor-pressure measurements but, also, the uncertainties in the heats of sublimation of hafnium and boron.

It is to be noted that to have a more positive heat of formation for  $\text{HfB}_2$ , the heat of sublimation of either Hf or B would have to be increased. Since the vaporization data for  $\text{HfC}$ , discussed elsewhere, also gave a rather negative heat of formation for  $\text{HfC}$ , it is possible that the heat of sublimation for Hf should be increased numerically by 5 to 10 kcal/mole. However at the present time, insufficient data are available to settle this question.

At this time, the data for the heat of formation of  $\text{HfB}_2$  seem to range from -75 to -85 kcal/mole. Accordingly an intermediate value is chosen, and  $\Delta H_{f298.15}^\circ = -80.0$  kcal/mole is accepted. In the table prepared using this value, it is found that  $\Delta F_{1700^\circ\text{K}}^\circ = -75.466$  kcal/mole. As noted earlier, Rudy and Benesovsky<sup>8</sup> have indicated that the free energy of formation of  $\text{HfB}_2$  at  $1673^\circ\text{K}$  should be more negative than -80 kcal/mole. For the present calculations to be consistent with their observation, the heat of formation of  $\text{HfB}_2$  should be at least -85.0 kcal/mole or more negative.

However at the present time, it is felt that the accepted data herein give reasonable agreement with available experimental data. As soon as the new low-temperature heat-capacity data and heat-of-formation data<sup>15</sup> become available, a more accurate table can be prepared. It is believed that the present heat-of-formation value is subject to an uncertainty of  $\pm 5$  kcal/mole.

#### Supplement

Westrum<sup>22</sup> found experimentally that  $S_{298.15}^\circ$  for  $\text{HfB}$  is 10.24 e. u.,  $C_{p, 298.15}^\circ = 11.89$  cal deg  $\text{K}^{-1}$  gfw<sup>-1</sup>, and  $H_{298.15}^\circ - H_0^\circ = 1766$  cal gfw<sup>-1</sup>. The data agree fairly well with the estimate used in the present work. The data were received too late for inclusion in the present tables. Trulson and Goldstein<sup>23</sup> performed mass-spectrometric vaporization studies of  $\text{HfB}_2$ . Their preliminary analysis yielded a heat of formation  $\Delta H_{f298.15}^\circ = -61$  kcal/mole.

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## 9.2 Hafnium Carbides

A detailed analysis is presented for hafnium carbide. In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

### 9.2.1 Hafnium Carbide ( $\text{HfC}_{(s)}$ )

#### a. Phase Diagram, Crystal Structure, and Melting Point

A recent phase diagram for the Hf-HfC system has been given by Avarbe et al.<sup>1</sup> Earlier work has been summarized by Storms,<sup>2</sup> who has referred to the work of Benesovsky and Rudy.<sup>3</sup> From this earlier work, a maximum melting temperature of 3900°C is shown for  $\text{HfC}_{1.0}$ , consistent with Agte and Alterthum<sup>4</sup> value of 3887°C. For the HfC-C eutectic, Cotter and Kohn<sup>5</sup> reported 2800°C, Portnoi et al.<sup>6</sup> reported 3250°C, Krikorian<sup>7</sup> reported 2915°C, and Benesovsky and Rudy<sup>3</sup> found 3000°C.

For the Hf-HfC eutectic, Krikorian<sup>7</sup> found 2150°C, and Benesovsky and Rudy<sup>3</sup> showed an estimated value of 2000°C on their diagram. In disagreement with such data and hypothetical diagrams of Samsonov and Portnoi<sup>8</sup> and Nowotny et al.,<sup>9, 10</sup> Avarbe et al.<sup>1</sup> found a peritectic in the Hf-HfC system at  $2820^\circ \pm 50^\circ\text{C}$ . At this temperature, the  $\alpha$ -Hf phase containing 18-atom-percent carbon decomposes into liquid and an HfC phase containing 35-atom-percent carbon. They studied melting of alloys from 11.8 to 47.6-atom-percent carbon. At this latter composition, they reported a melting point of  $3520^\circ \pm 30^\circ\text{C}$ . On their phase diagram, they have used the value of 3890°C as the melting point of  $\text{HfC}_{1.0}$ , presumably based on the Agte and Alterthum<sup>4</sup> data. Other possible sources for phase data in the Hf-C system, which were checked but failed to have any data, were the works of Vickery and Muir,<sup>11</sup> and Kaufmann et al.<sup>12</sup> Additional phase data have been obtained by Nowotny et al.<sup>13</sup> for the Hf-B-C system, and by Benesovsky and Rudy.<sup>14</sup>

The HfC phase has an fcc (NaCl-type) structure. This phase persists from  $\text{HfC}_{0.54}$  or  $\text{HfC}_{0.59}$  to  $\text{HfC}_{1.0}$ , at 1500°C according to Benesovsky and Rudy.<sup>3</sup> The phase diagram of Avarbe et al.<sup>1</sup> is consistent with these data. Thus, in the entire Hf-C system excluding the terminal elemental phases, there appears to be only the cubic HfC phase having a relatively wide range of homogeneity.

A lattice parameter of 4.641Å for the HfC phase has been obtained by Cotter and Kohn<sup>5</sup> for the  $\text{HfC}_{1.0}$  composition, by extrapolation. This value has been suggested to be the most accurate by Storms.<sup>2</sup> At the lower phase limit, the lattice parameter is about 4.61Å, from the work of Benesovsky and Rudy.<sup>3</sup> The recent work of Avarbe et al.<sup>1</sup> shows lattice parameters varying from 4.62 to 4.637Å as compositions varied

from 42 to 48 atom percent carbon. A plot of their data is in general agreement with the Benesovsky and Rudy data.

The melting point of 3887°C (4160°K) reported by Agte and Alterthum<sup>4</sup> appears to be the only experimental determination for the HfC<sub>1.0</sub> composition. Recently, Bowman<sup>15</sup> suggested that the relatively low eutectic in the Hf-C system indicates that the melting point is a few hundred degrees lower than the Agte and Alterthum<sup>4</sup> value.

If one linearly extrapolates the Avarbe et al<sup>1</sup> melting data to the HfC<sub>1.0</sub> composition, one obtains a melting temperature of about 3600°C or about 3900°K. In view of these recent indications therefore, a value for the melting point of HfC of 3900°K has been accepted. Clearly, this is subject to considerable uncertainty.

## b. Thermodynamic Properties

### 1) Low-temperature heat capacity and entropy at 298.15°K

For the present work, it was necessary to use an estimated value of entropy at 298.15°K since no experimental low-temperature heat-capacity data were available. The procedure used follows a scheme similar to that used for TiB<sub>2</sub>. Using a melting point of 3900°K for HfC as discussed earlier, and density data from Hansen and Anderko,<sup>16</sup> the effective Debye temperature of Hf and C in HfC were computed to be 268.1° and 1412.5°K, respectively. The calculations also lead to  $C_{p,298.15}^{\circ} = 8.228 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^{\circ} = 9.852 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  and  $H_{298.15}^{\circ} - H_0^{\circ} = 1.494 \text{ kcal gfw}^{-1}$ . It is believed that all of these quantities are accurate to about 5 percent.

Most other estimation procedures only tabulate  $S_{298}^{\circ}$  values. Thus, Kelley<sup>17</sup> found  $S_{298}^{\circ} = 10.9 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ , and Krikorian<sup>18</sup> found  $S_{298}^{\circ} = 9.9 \pm 0.5 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ . The latter value is in excellent agreement with the estimate herein.

### 2) High-temperature heat capacity

Until recently, there had been no experimental high-temperature heat capacity data for HfC. Kelley<sup>19</sup> had estimated high-temperature heat capacities. More recently, Coffman et al<sup>20</sup> and Neel et al<sup>21</sup> have obtained high-temperature heat capacities by means of drop calorimetry. The Coffman et al data have covered the lower-temperature region (440° to 1367°K), while the Neel et al data have spanned a much wider range (540° to 3016°K).

In the present work, the Shomate<sup>22</sup> method to evaluate the above data has been used. A value of  $C_{p,298}^{\circ} = 8.228 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  was chosen from the data estimated earlier. From the Shomate plot, an equation for the high-temperature heat capacity was found to be

$$C_p^{\circ} = 11.3404 + 1.30 \times 10^{-3}T - 3.1112 \times 10^{-5}T^{-2} \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}. \quad (\text{IVB9. 2})$$

This equation was then used to compute free-energy functions to 3900°K. It is of interest to compare these data with calculations based on the Debye functions mentioned earlier.

TABLE 27

COMPARISON OF ESTIMATED AND EXPERIMENTAL DATA FOR HfC

T	$C_p^{\circ}$ , Exptl	$C_p^{\circ}$ , Debye	$S^{\circ}$ , Exptl	$S^{\circ}$ , Debye
°K	cal deg K <sup>-1</sup> gfw <sup>-1</sup>		cal deg K <sup>-1</sup> gfw <sup>-1</sup>	
298.15	8.228	8.228	9.852	9.852
500	10.746	10.293	14.850	14.657
1000	12.329	12.158	22.894	22.489
1500	13.152	13.062	28.055	27.598
2000	13.863	13.889	31.938	31.467
2500	14.341	14.852	35.104	34.666

It is seen that the Debye function-estimation procedure gives data in relatively good agreement with experimental data. The inference may thus be made that the entropy estimate obtained by this procedure is also fairly reliable.

### 3) Heat of formation

As yet, there does not appear to have been any experimental determinations of the heat of formation of HfC. Various estimates have been made as follows:

$$\Delta H_{f29815, \text{HfC}}^{\circ} = -44.7 \text{ kcal gfw}^{-1} \quad \text{by Kelley and King, }^{23}$$

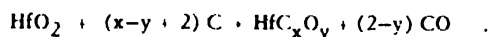
$$\Delta H_{f29815, \text{HfC}}^{\circ} = -47.0 \text{ kcal gfw}^{-1} \quad \text{by Krikorian, }^{24}$$

$$\Delta H_{f29815, \text{HfC}}^{\circ} = -50.0 \text{ kcal gfw}^{-1} \quad \text{by Ormont, }^{25} \text{ and}$$

$$\Delta H_{f29815, \text{HfC}}^{\circ} = -81.0 \text{ kcal gfw}^{-1} \quad \text{by Samsonov. }^{26}$$

Zhelankin, Kutsev, and Ormont<sup>27</sup> have reported equilibrium data for the reduction of  $\text{HfO}_2$  by carbon to form  $\text{HfC}$  and carbon monoxide for the range of 1743° to 2033°K. They indicate that the  $\text{HfO}_2$  is present as the monoclinic form although Curtis, Doney, and Johnson<sup>28</sup> have shown that monoclinic  $\text{HfO}_2$  is transformed into tetragonal  $\text{HfO}_2$  at 1973°K. It is possible that carbon stabilizes the monoclinic form of  $\text{HfO}_2$  for the experiments which Zhelankin et al<sup>27</sup> performed above 1973°K.

In their work, Zhelankin et al<sup>27</sup> have considered the equilibrium to be monovariant and represented by the following equation:



From a plot of the  $\log P_{\text{CO}}$  versus  $\frac{1}{T}$ , they have derived a heat of reaction  $\Delta H^\circ = +132 \pm 3 \text{ kcal gfw}^{-1}$ . If the assumption is made that  $x = 1$  and  $y = 0$ ; i. e., if it is assumed that  $\text{HfC}_x\text{O}_y$  is essentially pure  $\text{HfC}$ , then the reported data can be used to calculate the heat of formation of  $\text{HfC}$ . Some justification for this assumption can be provided from available lattice constant data for  $\text{HfC}$ ; refer to table 28.

Storms<sup>2</sup> has pointed out that oxygen, nitrogen, or a carbon-deficient structure lowers the lattice constant, whereas zirconium can raise it. The data for the specimens of Zhelankin et al<sup>27</sup> show lattice parameters close to these reported for pure grades of  $\text{HfC}$ .

In further work, Zhelankin, Kutsev, and Ormont<sup>32</sup> (1961) have reported analytical data for the composition of the carbide phases which Zhelankin et al<sup>27</sup> had reported in 1959. In the 1961 report, they indicated that the mean composition is  $\text{HfC}_{0.95}\text{O}_{0.05}$  for specimens equilibrated in the temperature range of 1743 to 2003°K. This work, thus, substantiates the conclusion already reached that the composition of the carbide must be near the stoichiometric one. However, to proceed further and assign an activity of unity to  $\text{HfC}$  is a further extrapolation which cannot be completely verified at this time. It is also to be noted that Zhelankin et al<sup>32</sup> in 1961 calculated a heat of formation at 298.15°K for  $\text{HfC}_{0.95}\text{O}_{0.05}$  of -73,700 cal/mole. They did not report a heat of formation for stoichiometric  $\text{HfC}$  free of oxygen.

TABLE 28

## LATTICE PARAMETERS FOR HAFNIUM CARBIDE

Reference	Type of Specimen	Lattice Parameter	
		kX	Å
Zhelankin <u>et al</u> <sup>27</sup>	{ 2003°K and P <sub>CO</sub> = 737 mm 1743°K and P <sub>CO</sub> = 59 mm	4.627 <sub>2</sub>	4.6365
		4.626 <sub>5</sub>	4.6358
Curtis <u>et al</u> <sup>28</sup>			4.646
Cotter and Kohn <sup>5</sup>			4.641
Meerson and Krein <sup>29</sup>	{ Percent C (combined)=6.27 Percent C (combined)=6.09 Percent C (combined)=5.99		4.63
			4.62
			4.61
Glaser <u>et al</u> <sup>30</sup>			4.64 ± 0.02
Nowotny, Rudy, and Benesovsky <sup>13</sup>			4.632
Benesovsky and Rudy <sup>3</sup>			4.628
Avarbe <u>et al</u> <sup>1</sup>			4.64
Coffman, Kibler, Lyon, and Acchione <sup>31</sup>			4.6435

Other work on the nature of the Hf-C-O system is given by Samsonov and Paderno,<sup>33</sup> who indicated that an HfO<sub>2</sub> reduction at 1000 to 1200°C yields Hf<sub>2</sub>O<sub>3</sub>. Higher temperatures of 1300° to 1800°C yield HfC<sub>x</sub>O<sub>y</sub> solid solutions. Between 1800° and 2000°C, HfC is formed with a lattice deficient in carbon. Thus, this evidence tends to indicate the activity of HfC may be somewhat less than unity because of the HfC<sub>x</sub>O<sub>y</sub> solid solution. Realizing this possible shortcoming, it still appears appropriate to make calculations of the Zhelankin et al<sup>27</sup> data, assuming that the activity of HfC is unity in the HfC<sub>x</sub>O<sub>y</sub> solid solution.

Using the Second-Law data already given and assuming the reaction to be  $\text{HfO}_2 + 3\text{C} \rightarrow \text{HfC} + 2\text{CO}$ , one may assume that the heat of the above reaction at 2000°K is  $\Delta H_{2000^\circ\text{K}}^\circ, \text{ reaction} = 132 \text{ kcal gfw}^{-1}$ . Then, using data for HfO<sub>2</sub> from the present report and data for CO from the JANAF tables,<sup>34</sup>

$$\begin{aligned} \Delta H_{\text{HfC formation}, 2000^\circ\text{K}}^\circ &= \Delta H_{\text{reaction}, 2000^\circ\text{K}}^\circ + \Delta H_{\text{f}, \text{HfO}_2, 2000^\circ\text{K}}^\circ - 2 \Delta H_{\text{f}, \text{CO}, 2000^\circ\text{K}}^\circ \\ &= 132 + 258.939 - 2(-28.372), \\ &= -70.195 \text{ kcal mole}^{-1}. \end{aligned}$$

Converting to 298.15°K gives  $\Delta H_{\text{HfC formation}, 298.15}^\circ = -68.676 \text{ kcal/mole}$ . This conversion has been made using enthalpy-content data for Hf, HfC, and C from the present project.

Next, a Third-Law analysis of the Zhelankin et al<sup>27</sup> data was performed. They had tabulated pressures for five different temperatures. Free-energy functions were used for HfO<sub>2</sub>, HfC, and C from the present project, and for CO from the JANAF tables.<sup>34</sup> Results of the calculations are summarized in table 29.

In table 29, the calculation of the heat of formation of HfC is completed by using data for HfO<sub>2</sub> from the present report and data for CO from the JANAF tables.<sup>34</sup>

TABLE 29

## SUMMARY OF THIRD-LAW CALCULATIONS FOR REACTION



Temperature °K	P <sub>CO</sub> atm	(fef) <sup>°</sup> HfO <sub>2</sub> cal deg K <sup>-1</sup> gfw <sup>-1</sup>	(fef) <sup>°</sup> C cal deg K <sup>-1</sup> gfw <sup>-1</sup>	(fef) <sup>°</sup> HfC cal deg K <sup>-1</sup> gfw <sup>-1</sup>	(fef) <sup>°</sup> CO cal deg K <sup>-1</sup> gfw <sup>-1</sup>	ΔH <sup>°</sup> <sub>298.15</sub> kcal/mole
1743	0.077632	30.4337	4.9260	20.0519	54.1119	162.485
1828	0.221053	31.1834	5.1175	20.5326	54.4238	162.405
1913	0.447368	31.9110	5.3042	20.9983	54.7266	164.183
2003	0.969737	32.6751	5.4963	21.4767	55.0361	165.261
2033	1.309210	32.9390	5.5590	21.6330	55.1370	165.120
Average						163.891

$$\bullet \text{fef} = - \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right)$$

$$\Delta H_{\text{HfC, formation, 298.15}}^\circ = \Delta H_{\text{reaction, 298.15}}^\circ - \Delta H_{\text{f, HfO}_2}^\circ - 2 \Delta H_{\text{f, CO}}^\circ$$

$$163.891 = (-2(6.060)) - 2(-36.417)$$

$$\bullet = -49.335 \text{ kcal/mole.}$$

It is seen that rather different values are obtained for the heat of formation of HfC, depending on whether a Second- or Third-Law treatment is used. Because of the difficulty of obtaining accurate temperature coefficients at such high temperatures, it is believed that the Third-Law data are more reliable although, of course, still subject to the assumption that activities of  $\text{HfO}_2$ , C, and HfC are unity. Thus from the Zhelankin *et al.*<sup>27</sup> data, the value of  $\Delta H_{f,298.15,\text{HfC}}^\circ = -49.335$  kcal/mole is preferred. It can be noted that if the activity of HfC is less than unity, then the effect will be to make  $\Delta H_{f,298.15,\text{HfC}}^\circ$  more positive, whereas, if the activity of  $\text{HfO}_2$  is less than unity, then the heat of formation of HfC will be more negative.

Vaporization data for HfC were presented by Coffman *et al.*<sup>31</sup> Hot-pressed specimens were subjected to weight-loss experiments. From carbon analyses of the sublimate, from constant values of the lattice parameter of the test specimen, and from the constant combined carbon content of the specimens, it was concluded that stoichiometric HfC vaporizes congruently. The vaporization was considered to be into gaseous hafnium and carbon.

The results of a Third-Law analysis of the Coffman *et al.*<sup>31</sup> vaporization data using their tabulated pressures (p. 88) are shown in table 30. Free-energy-function data for HfC, Hf, and  $\text{C}_{(g)}$  are from this project.

From the average heat of vaporization of HfC in table 30, according to the reaction  $\text{HfC} \rightarrow \text{Hf}_{(g)} + \text{C}_{(g)}$ , it is possible to calculate the heat of formation of HfC at 298.15°K from the equations:

$$\Delta H_{f,\text{HfC},298.15}^\circ = \Delta H_{f,\text{Hf}(g),298.15}^\circ + \Delta H_{f,\text{C}(g),298.15}^\circ - \Delta H_{\text{re},298.15}^\circ$$



TABLE 30

ANALYSIS OF HAFNIUM CARBIDE VAPORIZATION DATA FOR REACTION  $\text{HfC}_{(s)} \rightarrow \text{Hf}_{(g)} + \text{C}_{(g)}$ 

Temperature	$P_{\text{Hf}}$	$P_{\text{C}}$	$(f_{\text{HfC}})^*$	$(f_{\text{Hf}})^*$	$(f_{\text{C}})^*$	$\Delta H_{298.15}^*$
$^{\circ}\text{K}$	atm	atm	cal deg $\text{K}^{-1}$ gfw $^{-1}$	cal deg $\text{K}^{-1}$ gfw $^{-1}$	cal deg $\text{K}^{-1}$ gfw $^{-1}$	kcal/mole
2313	$2.291 \times 10^{-10}$	$6.026 \times 10^{-11}$	23.0198	51.2767	43.6184	376.443
2365	$4.467 \times 10^{-10}$	$1.177 \times 10^{-10}$	23.2645	51.4025	43.7150	378.569
2369	$6.310 \times 10^{-10}$	$1.660 \times 10^{-10}$	23.2832	51.4121	43.7224	375.960
2372	$8.318 \times 10^{-10}$	$2.138 \times 10^{-10}$	23.2971	51.4193	43.7279	373.938
2386	$1.072 \times 10^{-9}$	$2.818 \times 10^{-10}$	23.3622	51.4527	43.7535	373.618
2404	$9.333 \times 10^{-10}$	$2.455 \times 10^{-10}$	23.4454	51.4955	43.7862	377.739
2427	$1.585 \times 10^{-9}$	$4.074 \times 10^{-10}$	23.5512	51.5500	43.8279	376.332
2446	$2.042 \times 10^{-9}$	$5.248 \times 10^{-10}$	23.6380	51.5948	43.8620	376.797
2451	$1.698 \times 10^{-9}$	$4.467 \times 10^{-10}$	23.6608	51.6066	43.8710	379.246
2463	$2.692 \times 10^{-9}$	$6.918 \times 10^{-10}$	23.7152	51.6347	43.8924	376.694
2496	$4.169 \times 10^{-9}$	$1.096 \times 10^{-9}$	23.8640	51.7117	43.9509	377.256
2529	$5.754 \times 10^{-9}$	$1.479 \times 10^{-9}$	24.0117	51.7878	44.0087	379.083
2523	$6.310 \times 10^{-9}$	$1.660 \times 10^{-9}$	23.9849	51.7740	43.9983	377.149
2535	$6.310 \times 10^{-9}$	$1.660 \times 10^{-9}$	24.0384	51.8015	44.0192	378.930
2569	$1.096 \times 10^{-8}$	$2.818 \times 10^{-9}$	24.1889	51.8790	44.0780	378.455
2634	$2.455 \times 10^{-8}$	$6.310 \times 10^{-9}$	24.4726	52.0251	44.1884	379.518
2650	$2.951 \times 10^{-8}$	$7.586 \times 10^{-9}$	24.5416	52.0607	44.2152	379.867
2720	$7.080 \times 10^{-8}$	$1.862 \times 10^{-8}$	24.8398	52.2145	44.3309	380.239
2724	$8.511 \times 10^{-8}$	$2.188 \times 10^{-8}$	24.8567	52.2232	44.3374	378.924
2824	$2.692 \times 10^{-7}$	$6.918 \times 10^{-8}$	25.2741	52.4368	44.4992	379.793
2867	$4.169 \times 10^{-7}$	$1.096 \times 10^{-7}$	25.4502	52.5272	44.5668	380.411
2881	$4.898 \times 10^{-7}$	$1.288 \times 10^{-7}$	25.5071	52.5564	44.5886	380.405
2933	$7.943 \times 10^{-7}$	$2.042 \times 10^{-7}$	25.7167	52.6642	44.6689	381.703
2942	$9.772 \times 10^{-7}$	$2.512 \times 10^{-7}$	25.7528	52.6827	44.6827	380.441
2961	$1.175 \times 10^{-6}$	$3.090 \times 10^{-7}$	25.8285	52.7216	44.7118	380.572
3003	$1.549 \times 10^{-6}$	$3.981 \times 10^{-7}$	25.9948	52.8070	44.7755	382.757
3044	$3.162 \times 10^{-6}$	$8.128 \times 10^{-7}$	26.1557	52.8893	44.8367	379.296
3085	$5.129 \times 10^{-6}$	$1.318 \times 10^{-6}$	26.3150	52.9705	44.8971	378.421
3145	$7.763 \times 10^{-6}$	$1.995 \times 10^{-6}$	26.5455	53.0882	44.9846	380.520

$$*f_{\text{ef}} = - \left( \frac{F_{\text{T}}^{\circ} - H_{298}^{\circ}}{T} \right)$$

average  $\Delta H_{\text{reaction}, 298.15}^{\circ} = 378.589$

Thus, using data for  $\text{Hf}_{(g)}$ ,  $\text{HfC}_{(s)}$  and  $\text{C}_{(g)}$  developed here, the heat of formation is found as:

$$\Delta H_{f, \text{HfC}, 298.15}^{\circ} = 144.924 + 170.890 - 378.589 \\ = -62.775 \text{ kcal/mole.}$$

Bolgar *et al*<sup>35</sup> have reported a heat of vaporization of only 139.64 kcal/mole as contrasted with the value of 378.589 kcal/mole found by Coffman *et al*.<sup>31</sup> The data of Bolgar *et al* appear subject to serious error. Also, they consider vaporization to yield molecular species rather than atomic species. Hence, their data have not been further considered here.

A third type of experimental data for the heat of formation of  $\text{HfC}$  is that obtained by Kelley<sup>36</sup> by combustion calorimetry. This value is still a provisional value subject to change because of inadequate specimen purity. The value found is  $\Delta H_{f298.15}^{\circ} = -59.0$  kcal/mole.

To summarize the available experimental data, it is seen that  $\text{Hf-C-O}$  equilibria yield a Third-Law value of  $\Delta H_{f\text{HfC}}^{\circ} = -49.335$  kcal/mole, vaporization data give  $-62.775$  kcal/mole, and the preliminary combustion data give  $-59.0$  kcal/mole. It is clear that the agreement is not good. Also, it can be noted that most estimates have favored a value near  $\Delta H_{f298.15}^{\circ} = -50$  kcal/mole. For the present purposes, it is felt that an average value is probably the best choice. Accordingly, a rounded value of  $\Delta H_{f\text{HfC}, 298.15}^{\circ} = -55.0$  kcal/mole is accepted. Clearly, this is subject to an appreciable uncertainty of at least  $\pm 5$  kcal/mole.

#### 4) Uncertainties

Uncertainties in the thermodynamic functions for  $\text{HfC}$  were calculated by assuming an uncertainty in the entropy at  $298.15^{\circ}\text{K}$  of  $\pm 0.5$  e. u. Uncertainties in heat capacities were also estimated as indicated in the table of uncertainties.

#### Supplement

Trulson and Goldstein<sup>37</sup> studied the  $\text{HfB}_2 + \text{C} \rightarrow \text{HfC} + 2\text{B}_{(g)}$  equilibria and indicated that the heat of formation of  $\text{HfC}$  is about  $-50$  kcal/gfw<sup>-1</sup>. Rudy and Nowotny<sup>38</sup> from a study of the  $\text{Hf-Ta-C}$  system at  $1850^{\circ}\text{C}$  ( $2123^{\circ}\text{K}$ ) found that  $\Delta F_{\text{HfC}}^{\circ} - \Delta F_{\text{TaC}}^{\circ} = -8.5$  kcal/gfw<sup>-1</sup>. Using data from this report for  $\text{TaC}$ , a heat of formation for  $\text{HfC}$  of  $\Delta H_{f298.15}^{\circ} = -48.5$  kcal/mole is indicated. Engelke *et al*<sup>39</sup> found a melting point of  $3890^{\circ}\text{C}$  ( $4163^{\circ}\text{K}$ ) which is somewhat larger than the value accepted here.

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### 9.3 Hafnium Nitrides

#### Phase Diagram and General Information

There do not appear to have been sufficient studies of the Hf-N system to yield a complete phase diagram. Hansen and Anderko<sup>1</sup> note that the only compound found is HfN with an fcc structure. Storms<sup>2</sup> also notes the lack of data for the Hf-N system. He does cite the work of Rudy and Benesovsky<sup>3</sup> which indicates that HfN and Hf<sub>2</sub>N phases exist. Storms<sup>2</sup> considers the latter phase (Hf<sub>2</sub>N) unlikely. However, in view of some recent work by Nowotny et al.,<sup>4</sup> and Holmberg,<sup>5</sup> which favors a Ti<sub>2</sub>N phase in the analogous Ti-N system, it may be possible that an Hf<sub>2</sub>N phase does exist.

In the present work, there appear to be sufficient data to develop a thermodynamic table for the HfN composition. However, for other compositions and other possible phases such as the Hf<sub>2</sub>N phase, there are still insufficient thermodynamic data.

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#### 9.3.1 Hafnium Nitride (HfN<sub>(s,l)</sub>)

##### a. Crystal Structure and Melting Points

According to Hansen and Anderko,<sup>1</sup> the phase HfN has a metallic character and an fcc structure of the NaCl (B1) type. From the work of Glaser et al.,<sup>2</sup> the lattice parameter is  $a = 4.52\overset{\circ}{\text{A}}$ . Kibler et al.<sup>3</sup> found the lattice parameter to be  $a = 4.521\overset{\circ}{\text{A}}$  and noted that it remained essentially constant over the homogeneity range. Rudy and Benesovsky<sup>4</sup> found the lattice parameter to be  $4.524\overset{\circ}{\text{A}}$  at 42.6 atom-percent N (HfN<sub>0.742</sub>),  $4.518\overset{\circ}{\text{A}}$  at HfN<sub>1.0</sub>, and  $4.515\overset{\circ}{\text{A}}$  at 52.5 atom-percent N (HfN<sub>1.105</sub>). The last work gives the best representation of the homogeneity range for the HfN phase.

Miscellaneous physical properties for HfN have been given by Samsonov and Verkhoglyadova,<sup>5</sup> and Storms.<sup>6</sup> A melting point of 3310°C (3583°K) has been reported by Ruff.<sup>7</sup>

b. Thermodynamic Properties

1) Entropy and heat content at 298.15°K

Kelley and King<sup>8</sup> do not tabulate any experimental low-temperature heat-capacity data, but refer to a single estimate of  $S_{298.15}^{\circ} = 10.9 \pm 0.3$  e. u. by Kelley and King.<sup>9</sup> Kubaschewski and Evans<sup>10</sup> list a value of  $13.1 \pm 1.5$  e. u. In the present work, the Lindemann technique was used to estimate  $S_{298.15}^{\circ} = 11.487$  e. u.,  $C_{p, 298.15}^{\circ} = 9.794$  cal degK<sup>-1</sup> gfw<sup>-1</sup>, and  $H_{298}^{\circ} - H_0^{\circ} = 1.773$  kcal gfw<sup>-1</sup>. Another method of estimating the entropy can be made by reference to the analogous elemental Zr and ZrN tables. Here the values of  $S_{298.15}^{\circ}$  are identical; i. e., 9.29 e. u. By comparison with elemental Hf, one would thus expect the  $S_{298.15}^{\circ}$  to be 10.7 e. u. In the present work, this latter estimate is used. It is expected that this value is reasonably correct, but may need to be revised upward later to account for the defect structure of the compound lattice. The estimate of  $H_{298.15}^{\circ} - H_0^{\circ} = 1.773$  kcal gfw<sup>-1</sup> is the only one available and is used here.

2) High-temperature heat content

Kelley<sup>11</sup> lists only an estimated heat-capacity equation for HfN based on the work of Kelley and King.<sup>9</sup> The equation for the range 298° to 2000°K is

$$C_p^{\circ} = 9.84 + 2.22 \times 10^{-3}T \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

Experimental high-temperature heat-content measurements have been made by Neel *et al*<sup>12</sup> for the range 503° to 4750° F (534.8° to 2894.2°K). A later work by Pears *et al*<sup>13</sup> reported a different heat-capacity relation, but did not modify the original enthalpy data. In the present work, the original enthalpy data were converted to cgs units as shown herein. A correction of  $H_{298.15}^{\circ} - H_{273.15}^{\circ} = 250$  cal gfw<sup>-1</sup> was made to obtain the values shown on the following page. The correction (a minor one) was made by comparison with TiN and ZrN.

ENTHALPY DATA OF NEEL et al<sup>12</sup> CONVERTED  
TO cgs UNITS

T °K	$H_T^0 - H_{298.15}^0$ cal gfw <sup>-1</sup>
534.8	2391.6
842.0	6092.0
1084.8	9910.1
1363.7	14188.0
1622.0	17824.3
1955.3	22957.8
2213.7	26808.0
2513.7	29374.8
2755.3	33011.0
2810.9	33652.7
2894.2	37930.7

The foregoing data were treated by the Shomate method using  $C_p^0, 298.15 = 9.8 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ . This value was rounded off from the estimate of the previous section. The equation obtained was

$$C_p^0 = 10.936 + 2.2268 \times 10^{-3}T - 1.5950 \times 10^{-5}T^2 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation (when integrated) reproduces the original enthalpy data to 7.44 percent at 1363.7°K and better at all other experimental points. The equation is hence not very precise, but is probably reasonably correct. It is extrapolated in the present work to the melting point.

At the melting point, the heat of fusion is estimated to be 15.0 kcal gfw<sup>-1</sup>. The heat capacity of liquid HfN is estimated to be 16.0 cal degK<sup>-1</sup> gfw<sup>-1</sup>.

### 3) Heat of formation

Combustion calorimetry was used by Humphrey<sup>14</sup> to obtain a heat of formation for HfN of  $-88.24 \pm 0.34 \text{ kcal gfw}^{-1}$ . No corrections were made to these data since the heat of formation for HfO<sub>2</sub>



was consistent with the value used in this tabulation. No attempt was made to correct for deviation from stoichiometry. Thus, Storms<sup>6</sup> suggests that their composition was  $\text{HfN}_{1.03}$  although Humphrey stated that their sample had "virtually the correct composition."

Earlier, a value of  $\Delta H_{f29815}^\circ = -78.3 \text{ kcal gfw}^{-1}$  had been tabulated by Brewer et al.<sup>15</sup>

In the present work, the Humphrey<sup>14</sup> data have been accepted.

#### 4) Vaporization studies

Kibler et al.<sup>3</sup> have performed vaporization studies of  $\text{HfN}$  using the Knudsen method. Nitrogen gas is the gaseous species. Measurements were made at  $1931^\circ$ ,  $2133^\circ$ , and  $2356^\circ\text{K}$  for a range of compositions. Difficulty was experienced in obtaining reproducible results. It was considered that diffusion processes may have hampered the attainment of equilibrium.

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## 9.4 Hafnium Oxides

Detailed analyses were made for  $\text{HfO}(\text{g})$ ,  $\text{HfO}_2(\text{s}, \text{l})$  and  $\text{HfO}_2(\text{g})$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

### 9.4.1 Hafnium Monoxide ( $\text{HfO}(\text{g})$ )

#### a. Thermodynamic Functions

There are very little spectral data available to make accurate calculations of thermodynamic functions. Krishnamurty<sup>1</sup> in a brief note described a study of the  $\text{HfO}$  spectra. He interpreted the ground state to be  $^3\pi$  and found the multiplet splitting of this state gave term values as shown below:

State	Term Value
	$\text{cm}^{-1}$
$3\pi_2$	4003
$3\pi_1$	2084
$3\pi_0$	0

The multiplet splitting observed is much larger than for the  $\text{TiO}$  and  $\text{ZrO}$  molecules; however, this is consistent with the observation by Herzberg<sup>2</sup> (p. 216) that the coupling constant  $A$  increases rapidly with the number of electrons. The coupling constant is defined in Herzberg's equation (V, 8) as shown below:

$$T_e = T_o + A \Lambda \Sigma,$$

where

- $T_e$  = Electronic energy of a multiplet term,
- $T_o$  = Electronic energy of a term when spin is neglected,
- $A$  = Coupling constant,
- $\Lambda$  = Component of electronic orbital angular momentum along the internuclear axis, and
- $\Sigma$  = Component of electron spin along internuclear axis.

For  $\text{TiO}$  in its  $X^3\pi$  state, Herzberg gives values of  $A = 67$  to  $100$ . Values of  $A$  for  $\text{ZrO}$  are about  $300$ . Values of  $A$  for  $\text{HfO}$  are not given, but it is expected that they would be considerably larger, and, hence, be consistent with the observation of Krishnamurty.<sup>1</sup>

Further indication that the multiplet splitting in  $\text{HfO}$  is expected to be large can be obtained by reference to the energy levels of atomic  $\text{Hf}$  or  $\text{Hf}^{+2}$ . Energy levels for atomic  $\text{Hf}$  ( $\text{HfI}$ ) are given by Moore<sup>3</sup> as follows:

TABLE 31

## ENERGY LEVELS FOR ATOMIC HAFNIUM

Term	J	Level cm <sup>-1</sup>
a <sup>3</sup> F	2	0.0
	3	2356.68
	4	4567.64

From the large splitting observed for atomic Hf, it appears reasonable to expect splitting of the same order for the molecular HfO species.

The vibrational constant for the ground state of HfO was estimated by Krishnamurty<sup>1</sup> to give  $\omega_e = 865 \text{ cm}^{-1}$ . However, Brewer and Chandrasekharaiiah<sup>4</sup> also using an estimation procedure gave  $\omega_e = 895 \text{ cm}^{-1}$  and  $r_e = 1.74 \text{ \AA}$ . For their estimation procedure, they referred to neighboring molecules in the periodic table.

To make calculations, the analysis of Krishnamurty<sup>1</sup> has been accepted that the electronic ground state is  $X^3\pi$  with his term values. The rotational constant  $B_e$  has been derived from Brewer and Chandrasekharaiiah's data, and the vibrational constant given by them has also been accepted. It appears likely that there may be other low-lying electronic states for HfO by analogy with TiO and ZrO. However in view of the lack of data, no attempt is made to account for this possibility. It is clear that resulting calculations may be subject to appreciable uncertainty. The final accepted data are shown below.

TABLE 32

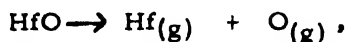
## SPECTROSCOPIC DATA USED FOR HfO CALCULATIONS

State	$T_e$ cm <sup>-1</sup>	$\omega_e$ cm <sup>-1</sup>	$B_e$ cm <sup>-1</sup>
$3\pi$	4003	895	0.3792
	2084		
	0		

## b. Heat of Formation

Brewer<sup>5</sup> had made an estimate of the dissociation energy of HfO(g). In a preface, he had asked that these data not be published because of their preliminary nature, and, accordingly, this value is not tabulated here. Ackermann and Thorn<sup>6</sup> have reported that the total vapor pressure of HfO<sub>2</sub> at 2940°K is  $3 \times 10^{-5} \text{ atm}$ .

They also reported a dissociation energy of  $8.0 \pm 0.3$  e.v. ( $184.504 \pm 7$  kcal) for  $\text{HfO}_{(g)}$  at  $0^\circ\text{K}$ . Thus, for the reaction,



$$\begin{aligned}\Delta H^\circ_{\text{HfO, formation}, 0^\circ\text{K}} &= \Delta H^\circ_{\text{Hf}} + \Delta H^\circ_{\text{fO}} - \Delta H^\circ_{\text{dissociation}} \\ &= 144.878 + 58.986 - 184.504 \\ &= +19.360 \text{ kcal/gfw.}\end{aligned}$$

In the above conversion, data for  $\text{Hf}_{(g)}$  and  $\text{O}_{(g)}$  have been taken from the present work. Vaporization studies for  $\text{HfO}_2$  have also been reported by Shchukarev and Semenov<sup>7</sup> who used a mass spectrometer to show that  $\text{HfO}$  is the most important gaseous species. Further studies on the  $\text{HfO}_2$  vaporization have been reported by Panish and Reif,<sup>8</sup> who reported a dissociation energy of  $182.6 \pm 6$  kcal/gfw in general agreement with the earlier data of Ackermann and Thorn.<sup>6</sup>

For a consistent calculation, it would be desirable to recalculate the three sources of data already cited. At report time, this was not possible. Therefore for the present preliminary calculations, the heat of formation derived from the data of Ackermann and Thorn<sup>6</sup> was accepted; i. e.,  $\Delta H^\circ_{\text{HfO}, 0^\circ\text{K}} = 19.360$  kcal/gfw.

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#### 9.4.2 Hafnium Dioxide ( $\text{HfO}_2(s,l)$ )

##### a. Phase Diagram, Crystal Structure, Transition and Melting Points

Until recently, there have not been extensive studies of the Hf-O system. Thus, Hansen and Anderko<sup>1</sup> list only a melting point of 2780°C (3053°K) for the dioxide ( $\text{HfO}_2$ ). In 1963, Rudy and Stecher<sup>2</sup> have published phase data for the Hf-O system. The dioxide is the most refractory material in the Hf-O system. In fact,  $\text{HfO}_2$  is one of the most stable oxides known. According to Ackermann and Thorn,<sup>3</sup>  $\text{HfO}_2$  is the least volatile of all oxides. Its melting point is also high but somewhat less than that for  $\text{ThO}_2$  which has a value of 3300°C (3573°K), according to Hausner and Friedemann.<sup>4</sup> Kornilov<sup>5</sup> indicates that  $\text{ThO}_2$  is more stable than  $\text{HfO}_2$ .

Recent publications which have summarized work on the hafnium-oxygen system or on  $\text{HfO}_2$  include the works of Thomas and Hayes,<sup>6</sup> Rudy and Stecher,<sup>2</sup> and Hausner and Friedemann.<sup>4</sup> In the present analysis, work is confined to the  $\text{HfO}_2$  compound.

A comprehensive study of the physical properties of pure  $\text{HfO}_2$  has been made by Curtis, Doney, and Johnson.<sup>7</sup> They showed that the monoclinic form of  $\text{HfO}_2$  is stable from low temperature to 1700°C (1973°K). At this temperature, a phase transition to the tetragonal  $\text{HfO}_2$  occurs. Such behavior is similar to that for  $\text{ZrO}_2$  which undergoes a similar transition but at a lower temperature of about 1100°C. In his review article, Brewer<sup>8</sup> states that the transition of monoclinic to tetragonal  $\text{HfO}_2$  occurs at 1205°K. However, no supporting evidence is cited. Brewer also mentions that impurities such as MgO can convert  $\text{HfO}_2$  into a cubic form. Apparently, this form only exists with impurities present as in the case of  $\text{ZrO}_2$ .

Lattice constants have been found by Curtis et al<sup>7</sup> at room temperature and 1640°C for the monoclinic form. They found  $a=5.11 \text{ \AA}$ ,  $b=5.14 \text{ \AA}$ ,  $c=5.28 \text{ \AA}$ , and  $\beta = 99^\circ 44'$  at room temperature; and  $a=5.21 \text{ \AA}$ ,  $b=5.15 \text{ \AA}$ ,  $c=5.43 \text{ \AA}$ , and  $\beta = 98^\circ 48'$  at 1640°C. Additional data for the monoclinic form have been found by Adam and Rogers,<sup>9</sup> who gave the values  $a=5.1156 \text{ \AA}$ ,  $b=5.1722 \text{ \AA}$ ,  $c=5.2948 \text{ \AA}$ , and  $\beta = 99^\circ 11'$ .

For the tetragonal form of  $\text{HfO}_2$ , Curtis et al<sup>7</sup> found  $a=5.14 \text{ \AA}$  and  $c=5.25 \text{ \AA}$  at 1920°C.

A melting point of  $2900^\circ \pm 25^\circ\text{C}$  ( $3173^\circ \pm 25^\circ\text{K}$ ) has been found by Curtis et al.<sup>7</sup> They also list earlier literature values of 2812°C by Henning,<sup>10</sup> 2774°C by Clausing,<sup>11</sup> and 2810°C from the National Research Council.<sup>12</sup>

For the present analysis, the transition temperature and melting point found by Curtis *et al*<sup>7</sup> have been accepted. These values are 1973°K and 3173°K, respectively.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

Low-temperature heat-capacity data for HfO<sub>2</sub> have been reported by Todd<sup>13</sup> for the range of 52.47° to 298.16°K. They found  $S_{298.16^\circ K} = 14.18 \pm 0.10$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> and  $C_p^\circ, 298.16^\circ K = 14.40$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>. The value of  $H_{298}^\circ - H_0^\circ$  has not been tabulated by Todd;<sup>13</sup> however, it has been computed here by numerical integration on a computer to be 2345 cal/mole. At the same time,  $S_{298.15}^\circ$  has been found to be 14.188 cal deg K<sup>-1</sup> gfw<sup>-1</sup> and is used here for consistency. Todd's data join smoothly with the high-temperature data to be discussed shortly and, hence, is accepted as reported.

### 2) High-temperature heat content

High-temperature heat-content data for HfO<sub>2</sub> have been reported by Orr<sup>14</sup> for the range of 298° to 1804°K. His data lead to

$$H_T^\circ - H_{298.15}^\circ = 17.39 T + 1.04 \times 10^{-3} T^2 + 3.48 \times 10^5 T^{-1}$$

$$\text{and} \quad -6444 \text{ cal gfw}^{-1},$$

$$C_p = 17.39 + 2.08 \times 10^{-3} T - 3.48 \times 10^5 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Additional heat-content data have been obtained by the drop technique over a very wide temperature range by Pears *et al*.<sup>15</sup> Their data covered the range of 711° to 4740°F (650.4° to 2888.7°K). Appropriate conversions of the Pears *et al* data have been made to give enthalpy in cal gfw<sup>-1</sup> rather than the tabulated Btu/lb. Since their heat-content data are referenced to 0°C (273.15°K), it has been necessary to subtract a value of  $H_{298.15}^\circ - H_{273.15}^\circ = 351.25$  cal/mole from their converted tabulated values, thus yielding  $H_T^\circ - H_{298.15}^\circ$  values. The value of  $H_{298.15}^\circ - H_{273.15}^\circ$  is a relatively small correction obtained by graphical integration of the Todd<sup>13</sup> data in this temperature range. The values of  $H_T^\circ - H_{298.15}^\circ$  from the Pears *et al* data are shown on the following page.



# CONVERSION OF THE PEARS et al<sup>15</sup> ENTHALPY DATA

Temperature	$H_T^\circ - H_{298.15}^\circ$
$^\circ\text{K}$	cal gfw <sup>-1</sup>
650.4	4993
1025.4	12864
1354.8	18044
1658.2	24289
1908.2	34440
1930.4	33095
1949.8	33914
2185.9	40006
2230.4	44813
2499.8	47421
2502.6	49900
2752.6	58694
2888.7	60998

It can be seen above that the Pears et al data give only four points definitely corresponding to the monoclinic form of  $\text{HfO}_2$ . The three points at 1908, 1930, and 1949 $^\circ\text{K}$  are already close to the expected transition point. The data from these points show considerable scatter; i. e., the enthalpy content at 1908 $^\circ\text{K}$  is 1345 cal greater than the next value at 1930 $^\circ\text{K}$ . This corresponds to a deviation of 3.9 percent which seems rather large. In general, the enthalpy contents obtained by Pears et al agree with the Orr data.<sup>14</sup> However for the present purposes, it appears that

for the monoclinic form of  $\text{HfO}_2$  to 1973°K, it is better to utilize only the Orr data.

To ensure smooth joining of the low-temperature Todd data with the high-temperature Orr data, a smoothing technique has been used on the originally reported Orr equation for  $C_p^\circ$  given earlier. The smoothing technique used involved reading in, as input, individual values of  $C_p^\circ$  calculated from Orr's equation at 500°, 1000°, 1500°, and 2000°K. At 298.15°K, 20 values of  $C_{p,298.15}^\circ = 14.40 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  have been read in to ensure "weighting" the input data and, thus, "force" the resulting heat-capacity equation to go through the value  $C_{p,298.15}^\circ = 14.40 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

A computer program using a least-squares fit to various expressions provided the desired output. Some of the expressions obtained are

$$C_p^\circ = 13.1319 + 4.6348 \times 10^{-3} T \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

(sum of deviations squared = 5.573),

$$C_p^\circ = 17.2346 + 2.1628 \times 10^{-3} T - 0.30930 \times 10^6 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

(sum of deviations squared = 0.0033),

$$C_p^\circ = 11.6438 + 1.0165 \times 10^{-2} T - 0.26862 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

(sum of deviations squared = 1.2894), and

$$C_p^\circ = 16.999 + 0.25423 \times 10^{-2} T - 0.29727 \times 10^6 T^{-2} \\ - 0.13760 \times 10^{-6} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

(sum of deviations squared = 0.000577).

It is seen that the final equation gives the "best fit." Normally, this would be expected since it contains one additional parameter which can be adjusted. The equation of the type used by Orr gives the next best fit and is used here to conform more closely to his original equation. According to this equation with the extrapolation to the accepted transition temperature is adopted.

$$C_p^\circ = 17.2346 + 2.1628 \times 10^{-3} T - 0.3093 \times 10^6 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

for  $298.15 \leq T \leq 1973^\circ\text{K}$ .

There have been no reported experimental data for the heat of transition of  $\text{HfO}_2$  from monoclinic to tetragonal. The only experimental heat-content data covering the transition temperature are that of Pears et al.<sup>15</sup> However in their treatment of the data, they do not mention or show a transition. For the present analysis, their data have been replotted along with the data already accepted for monoclinic  $\text{HfO}_2$ . A value of the heat of transition of about 3 kcal/mole at 1973°K appeared to be indicated. This value is subject to considerable uncertainty because of the scatter in the experimental data. As a second approach to determining the heat of transition, the analogous case for  $\text{ZrO}_2$  has been considered. For this material, Kelley<sup>16</sup> lists a heat of transition of 1420 cal at 1478°K. This corresponds to an entropy of transition of 0.96 cal deg  $\text{K}^{-1}$  gfw<sup>-1</sup>. Assuming the same entropy of transition for  $\text{HfO}_2$ , the heat of transition is estimated to be  $1973 \times 0.96 = 1894$  cal gfw<sup>-1</sup>. Brewer<sup>8</sup> states that the entropy of transition is 1.2 e. u. for  $\text{ZrO}_2$ . This would suggest that the heat of transition for  $\text{HfO}_2$  is  $1.2 \times 1973 = 2367$  cal gfw<sup>-1</sup>. Based on these estimates, a rounded value of 2500 cal gfw<sup>-1</sup> for the heat of transition is accepted.

For the tetragonal form of  $\text{HfO}_2$ , the heat-content data of Pears et al have been utilized. Data in the range of 2185° to 2888°K (see foregoing table) have been plotted versus T. Because of scatter in the data points, a linear function appeared adequate to represent  $H_T^\circ - H_{298.15}^\circ$  over the range 1973°K to the melting point. The value adopted leads to

$$C_p^\circ = 26.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1} \text{ for } 1973^\circ\text{K} \leq T \leq 3173^\circ\text{K}.$$

The value of the heat capacity found appears rather large for a 3-atom molecule and may indicate pre-melting phenomena in the  $\text{HfO}_2$ . However, the uncertainty in the data is still too great to make any definitive statements.

At the melting point of 3173°K, it is necessary to estimate the heat of melting. The entropy of fusion is estimated to be  $2.6 \times 3 = 7.8$  e. u., thus leading to a rounded value of 25,000 cal gfw<sup>-1</sup> as the heat of fusion.

For liquid  $\text{HfO}_2$ , there were no experimental heat-capacity data. It was therefore estimated by assuming that the liquid has the same heat capacity as the solid at and below the melting point. Thus, it was assumed that  $C_p^\circ = 26.0$  cal deg  $\text{K}^{-1}$  gfw<sup>-1</sup>.

The tabular data for  $\text{HfO}_2$  have been extrapolated to 6000°K.

### 3) Vaporization data

Vaporization studies for  $\text{HfO}_2$  have been reported by Ackermann and Thorn,<sup>3</sup> Panish and Reif,<sup>17</sup> and Shchukarev and Semenov.<sup>18</sup> The latter two works show that  $\text{HfO}$  is the primary species involved in vaporization phenomena. According to Bondarenko and Tsarev,<sup>19</sup> the boiling point of  $\text{HfO}_2$  is greater than  $4700^\circ\text{K}$ . Skinner, Beckett, and Johnston<sup>20</sup> give  $5673^\circ\text{K}$  as the boiling point. At relatively low temperatures,  $\text{HfO}_2$  can lose oxygen to form  $\text{HfO}_{2-x}$  where  $x$  is small. Studies of the effect of such changes on the electrical conductivity for the range of  $784^\circ$  to  $1297^\circ\text{C}$  have been made by Kofstad and Ruzicka.<sup>21</sup> Measurements of oxygen partial pressure in equilibrium with  $\text{Hf-O}$  alloys have been made by Komarek and Silver<sup>22, 23</sup> for temperatures of  $968^\circ$  to  $1230^\circ\text{K}$  and compositions containing 5.15 to 21.2-atom-percent oxygen. Their data have not included sufficiently high oxygen concentrations to reach the  $\text{HfO}_{2-x}$  phase.

### 4) Heat of formation

A calorimetric heat-of-combustion value of  $\Delta H_{1298.15}^\circ = -266.060 \pm 0.28 \text{ kcal gfw}^{-1}$  has been found by Humphrey<sup>24</sup> for  $\text{HfO}_2$ . This value is adopted herein. Earlier values of  $-271.0$  and  $-271.5 \text{ kcal gfw}^{-1}$  have been given by Roth and Becker,<sup>25</sup> and Rossini *et al*,<sup>26</sup> respectively. The value from Rossini *et al* is based on the Roth and Becker value.

Komarek and Silver<sup>22</sup> have noted that the partial molar free energies of the hafnium-oxygen system are less negative than those of the zirconium-oxygen system. This is somewhat unexpected since the accepted heat of formation (and also free energy of formation) of  $\text{ZrO}_2$  is more positive than the value for  $\text{HfO}_2$ . However, Komarek<sup>23</sup> has indicated that additional work checks the earlier work of Komarek and Silver.<sup>22</sup> He shows that the apparent discrepancy can be accounted for by the differing solubilities of oxygen in hafnium and zirconium. Whereas the solubility in  $\alpha\text{-Zr}$  is close to 30-atom-percent O, in  $\alpha\text{-Hf}$  it is only 20-atom-percent according to Rudy and Stecher.<sup>2</sup> Thus for an  $\text{Hf-O}$  alloy at 20-atom-percent and for a 30-atom-percent  $\text{Zr-O}$  alloy,  $\Delta F_{\text{O}, 1200^\circ\text{K}} = -107 \text{ kcal/g-atom oxygen}$ . These data show that the difference in integral free energies of formation of  $\text{ZrO}_2$  and  $\text{HfO}_2$  are relatively small as expected.

In a recent review article, Huber and Holley<sup>27</sup> have mentioned that further confirmation work is needed for the heat of formation of several oxides including  $\text{HfO}_2$ . Realizing that the data may need

further verification, the Humphrey<sup>24</sup> value is accepted. It is suggested that the uncertainty may be greater than the value reported, and, somewhat arbitrarily, a value of  $\pm 4$  kcal gfw<sup>-1</sup> is assigned here, thus giving, as the accepted heat of formation,  $\Delta H_{f298.15}^\circ = -266.06 \pm 4$  kcal gfw<sup>-1</sup>.

### c. Uncertainties

Uncertainties have been calculated by assuming the following uncertainties in the basic data.

Quantity	Uncertainty
$S_{298.15}^\circ$ , e. u.	$\pm 0.10$
$C_p^\circ$ (298.15° to 500°K), cal deg K <sup>-1</sup> gfw <sup>-1</sup>	$\pm 0.25$
$C_p^\circ$ (500° to 1000°K), cal deg K <sup>-1</sup> gfw <sup>-1</sup>	$\pm 0.50$
$C_p^\circ$ (1000° to 1973°K), cal deg K <sup>-1</sup> gfw <sup>-1</sup>	$\pm 1.00$
$\lambda_{\text{Transition}}$ (1973°K), cal gfw <sup>-1</sup>	$\pm 1000$
$C_p^\circ$ (1973° to 3173°K), cal deg K <sup>-1</sup> gfw <sup>-1</sup>	$\pm 3.00$
$\lambda_{\text{Melting}}$ (3173°K), cal gfw <sup>-1</sup>	$\pm 5000$
$C_p^\circ$ (3173° to 6000°K), cal deg K <sup>-1</sup> gfw <sup>-1</sup>	$\pm 3.00$
$\Delta H_{f298.15}^\circ$ , kcal gfw <sup>-1</sup>	$\pm 4.00$

### Supplement

Wolten<sup>28</sup> recently reported that the monoclinic--tetragonal transition is diffusionless (i. e., all atoms have the same neighbors in either phase). He considers the transformation to resemble martensitic phase changes. The hysteresis loop associated with the change has a width of about 20° or 30°C in the range 1547° to 1718°C.

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### 9.4.3 Hafnium Dioxide ( $\text{HfO}_2(\text{g})$ )

#### a. Thermodynamic Functions

There are no experimental determinations of the structure and other spectroscopic constants for the  $\text{HfO}_2$  molecule. Accordingly, estimates of these parameters are required in order to calculate the thermodynamic functions.

Brewer and Rosenblatt<sup>1</sup> have calculated free energy functions for  $\text{HfO}_2$  by assuming it to be a linear molecule. They estimated the Hf-O distance to be  $1.74 \text{ \AA}$  and the vibrational frequency for the monoxide,  $\text{HfO}$ , to be  $895 \text{ cm}^{-1}$ . They used valence bond theory to estimate the vibrational frequencies of  $\text{HfO}_2$ . Electronic contributions were estimated with an ionic model.

In the present case, calculations similar to those of Brewer and Rosenblatt have been performed. It has been assumed that O-Hf-O is a linear molecule of  $D_{\infty h}$  symmetry (symmetry number = 2). The vibrational frequency for the monoxide was also assumed to be  $895 \text{ cm}^{-1}$ . Assuming the same stretching force constant in the dioxide as in the monoxide, it is found that  $k_1 = 6.9288 \times 10^5 \text{ dyne/cm}$ . The stretching force constant was assumed to be  $0.034k_1$  as has been assumed for many triatomic molecules on this project. Using the valence bond theory, the following vibrational frequencies were estimated:

$$\omega_1 = 857.4 \text{ cm}^{-1} \text{ (Multiplicity = 1)}$$

$$\omega_2 = 242.8 \text{ cm}^{-1} \text{ (Multiplicity = 2)}$$

$$\omega_3 = 931.1 \text{ cm}^{-1} \text{ (Multiplicity = 1).}$$

From the assumed O-Hf distance of  $1.74 \text{ \AA}$ , a moment of inertia  $I = 16.085 \times 10^{-39} \text{ gm cm}^2$  and a rotational constant  $B_e = 0.174 \text{ cm}^{-1}$  were calculated.

By analogy to the  $\text{TiO}_2$  molecule for which the ionic model predicts that  $\text{Ti}^{+4}$  ion has only the ground state with a degeneracy of one, it is assumed that  $\text{HfO}_2$  will also act like a  $^1\Sigma$  state with no important excited electronic states.



## b. Heat of Formation

Brewer and Rosenblatt<sup>1</sup> estimated the dissociation energy of  $\text{HfO}_2(\text{g})$  to be  $360 \pm 20$  kcal/mole (15.60 eV) at 298.15°K. They do not list their auxiliary data. Using our tabulated values for the heat of formation of  $\text{Hf}(\text{g})$  and  $\text{O}(\text{g})$  at 298.15°K we can calculate the heat of formation of  $\text{HfO}_2(\text{g})$  as follows:

$$\begin{aligned}\Delta H_{\text{f};\text{HfO}_2(\text{g})}^{\circ}; 298.15 &= \Delta H_{\text{fHf}(\text{g})}^{\circ} + 2 \Delta H_{\text{fO}(\text{g})}^{\circ} - \Delta H_{\text{diss}}^{\circ} \\ &= 144.924 + 2(59.557) - 360\end{aligned}$$

$$\Delta H_{\text{f};\text{HfO}_2(\text{g})}^{\circ}; 298.15 = -95.962 \text{ kcal/mole.}$$

Ackermann and Thorn<sup>2</sup> derived a free energy equation for the formation of  $\text{HfO}_2(\text{g})$  in a manner similar to one they used for  $\text{ZrO}_2$ . Their equation is

$$\Delta F_{\text{f};\text{HfO}_2(\text{g})}^{\circ} = -81,000 + 4.0T \text{ cal/mole.}$$

The temperature range to be applied is presumably the same as for  $\text{ZrO}_2$ . Hence, their heat of formation for  $\text{HfO}_2(\text{g})$  is presumably  $\Delta H_{\text{f};\text{HfO}_2(\text{g})}^{\circ}; 2500^{\circ}\text{K} = -81.0$  kcal/mole.

Then,

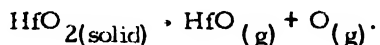
$$\begin{aligned}\Delta H_{\text{f};\text{HfO}_2(\text{g})}^{\circ}; 298.15 &= \Delta H_{\text{f}2500}^{\circ} + (H_{2500}^{\circ} - H_{298}^{\circ})_{\text{Hf}} + (H_{2500}^{\circ} - H_{298.15}^{\circ})_{\text{O}_2} \\ &\quad - (H_{2500}^{\circ} - H_{298.15}^{\circ})_{\text{HfO}_2} \\ &= -81.0 + 25.973 + 18.731 - 31.478\end{aligned}$$

$$\Delta H_{\text{f};\text{HfO}_2(\text{g})}^{\circ}; 298.15 = -67.774 \text{ kcal/mole.}$$

It should be noted here that, because of a melting point for hafnium at 2495°K, a calculation at temperatures below 2495°K would yield a heat of formation more negative by 5 kcal.

Panish and Reif<sup>3</sup> studied vaporization of  $\text{HfO}_2$ , but did not report observing  $\text{HfO}_2(\text{g})$ . Shchukarev and Semenov<sup>4</sup> used a mass spectrometer to study vaporization of hafnia from iridium cells. They reported that the  $\text{HfO}_2^+$  ion intensity was less than 0.01 that of  $\text{HfO}^+$  for 50-volt electrons. They also stated that  $\text{HfO}_2$  vaporizes differently than  $\text{ZrO}_2$  or  $\text{ThO}_2$ .

It is possible to make some rough approximations to derive a heat of formation for  $\text{HfO}_2(\text{g})$  from the observation of Shchukarev and Semenov.<sup>4</sup> First, it is assumed that their atmosphere was neutral, i. e., the reducing effect of the iridium cell is ignored. Utilizing this assumption, we can calculate the partial pressure of hafnium monoxide from the reaction



Using data for  $\text{HfO}_2(\text{solid})$ ,  $\text{HfO}(\text{g})$  and  $\text{O}(\text{g})$  from the present project,<sup>5</sup> we calculate a standard free energy of reaction at 2300°K of

$$\Delta F_{2300}^\circ = \Delta F_{\text{HfO}}^\circ + \Delta F_{\text{O}}^\circ - \Delta F_{\text{HfO}_2}^\circ$$

$$\Delta F_{2300}^\circ = -25570 + 24282 + 168193 - 166905 \text{ cal/mole.}$$

Therefore if  $P_{\text{HfO}} = P_{\text{O}}$ , then  $P_{\text{HfO}} = 10^{-7.929}$  atm. The observation of Shchukarev and Semenov<sup>4</sup> regarding ion current intensities is interpreted to yield  $P_{\text{HfO}_2} = 0.01 P_{\text{HfO}}$ . With this assumption,  $P_{\text{HfO}_2} \cong 10^{-10}$  atm at 2300°K. Then the free energy of sublimation for the reaction  $\text{HfO}_2(\text{solid}) \rightarrow \text{HfO}_2(\text{g})$  is

$$\Delta F_{2300}^\circ = 4.5758 \times 2300 \log P_{\text{HfO}_2}$$

$$\Delta F_{2300}^\circ = 105,243 \text{ cal/mole.}$$

A heat of sublimation of  $\text{HfO}_2(\text{g})$  at 298.15°K can now be calculated,

$$\begin{aligned} \Delta H_{298.15}^\circ &= \Delta F^\circ + T \left[ f_{\text{HfO}_2(\text{g})} - f_{\text{HfO}_2(\text{solid})} \right] \\ &= 105243 + 2300 \left[ 76.240 - 35.194 \right] \end{aligned}$$

$$\Delta H_{298.15}^\circ = 199,648 \text{ cal/mole.}$$

The heat of formation of  $\text{HfO}_2(\text{g})$  can next be calculated using the heat of formation of  $\text{HfO}_2(\text{solid})$  as -266.06 kcal/mole. We thus obtain a heat of formation for  $\text{HfO}_2(\text{g})$  as

$$\Delta H_{\text{f}; \text{HfO}_2(\text{g}); 298.15}^\circ = -266.06 + 199.648$$

$$= -66.412 \text{ kcal/mole.}$$

The agreement of this last heat-of-formation value with that derived from the Ackermann and Thorn<sup>2</sup> value must be considered rather fortuitous, but it is probable that the values are in the right range.

Accordingly, we accept an averaged, rounded value of  $\Delta H_f^\circ$  29815,  $\text{HfO}_2(\text{g})$  = -70.0 kcal/mole as the heat-of-formation. The uncertainty must be considered to be at least  $\pm 15$  kcal/mole.

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## 10. Iridium Compounds

The only iridium compounds investigated in this study were the oxides.

### 10.1 Iridium Borides

The borides of iridium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 10.2 Iridium Carbides

The carbides of iridium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 10.3 Iridium Nitrides

The nitrides of iridium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 10.4 Iridium Oxides

A detailed analysis was made for  $\text{IrO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 10.4.1 Iridium Oxide ( $\text{IrO}_{(g)}$ )

No spectroscopic data were available for gaseous  $\text{IrO}$ . The following values of  $\omega_e$  and  $r_e$  were estimated for this molecule.

$\omega_e (\text{cm}^{-1})$	$r_e (\text{\AA})$	$B_e (\text{cm}^{-1})$	$g$
790 (785)	1.84 (1.85)	0.335	4

Values in parentheses were estimated by Brewer and Chandrasekharaiah.<sup>1</sup>

$B_e$  was calculated from the estimated  $r_e$  by the relation

$$B_e = \frac{1.686 \times 10^{-15}}{\mu r_e^2} \quad (\text{IVB10.4.1-1})$$

where  $B_e$  is in units of  $\text{cm}^{-1}$ ,  $\mu$  is the reduced mass in atomic mass units, and  $r_e$ , the equilibrium internuclear distance, is in cm.

Thermodynamic functions of gaseous IrO were calculated with the above constants (equivalent to assuming a rigid rotator and harmonic oscillator), using only a ground electronic state with a statistical weight of 4.

From a study of the volatility of iridium in oxygen, Schäfer and Heitland<sup>2</sup> established that the product of the oxidation was IrO<sub>3</sub>(g). They found ΔH° to be 4.08 kcal/gfw for the reaction



at an average temperature of 1408°K. Alcock and Hooper<sup>3</sup> also studied this reaction in the temperature range from 1200° to 1400°K and reported an equilibrium constant which corresponded to a ΔH° of 4.15 kcal/gfw over the stated temperature range. Schäfer and Heitland<sup>2</sup> calculated ΔH°<sub>f298</sub> for this reaction to be 2.0 kcal/gfw from ΔH°<sub>f1408</sub>, an estimated heat-capacity equation for IrO<sub>3</sub>(g) and literature values for the heat capacities of Ir(s) and O<sub>2</sub>(g). Using this value for ΔH°<sub>f298</sub>, appropriate thermodynamic functions from the present compilation, and assuming H°<sub>298</sub> - H°<sub>0</sub> for IrO<sub>3</sub>(g) to be 3.2 kcal/gfw, the dissociation energy of IrO<sub>3</sub>(g) at 0°K, D°<sub>0</sub> was calculated to be 332 kcal/gfw. D°<sub>0</sub> for IrO(g) was assumed to be one-third of this quantity, or 111 kcal/gfw. This latter quantity corresponded to a ΔH°<sub>f298</sub> of 106 kcal/gfw to which an uncertainty of ± 15 kcal/gfw was assigned.

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## 11. Lanthanum Compounds

Detailed analyses were not made for these compounds.

### 11.1 Lanthanum Borides

The borides of lanthanum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 11.2 Lanthanum Carbides

The carbides of lanthanum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 11.3 Lanthanum Nitrides

The nitrides of lanthanum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 11.4 Lanthanum Oxides

The oxides of lanthanum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

## 12. Magnesium Compounds

The only magnesium compounds investigated in this study were the nitrides and oxides.

### 12.1 Magnesium Borides

The borides of magnesium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 12.2 Magnesium Carbides

The carbides of magnesium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 12.3 Magnesium Nitrides

A detailed analysis was made for  $\text{Mg}_3\text{N}_{2(s)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 12.3.1 Magnesium Nitride ( $\text{Mg}_3\text{N}_{2(s)}$ )

##### a. Phase Data, Crystal Structure, and Melting Point

Crystallographic data are available only for the  $\alpha$ , or low-temperature, phase of this compound, and it is a bcc, D5 structure with  $a = 9.95^1$  or  $9.93^2$  kX.

Enthalpy data of Mitchell<sup>3</sup> and Kelley<sup>4</sup> show the existence of two high-temperature phases; their transition temperatures and heats of transition are tabulated on the following page.

Sato<sup>5</sup> does not report these transitions, and since the discrepancy between the heat of the  $\alpha \rightarrow \beta$  transition shown above is small, it has been decided to use Mitchell's data in the calculation for these tables.

TABLE 33  
TRANSITIONS IN  $\text{Mg}_3\text{N}_2$

Transitions	Mitchell <sup>3</sup>		Kelley <sup>4</sup>	
	Temperature	$\Delta H_{\text{Trans}}$	Temperature	$\Delta H_{\text{Trans}}$
	$^{\circ}\text{K}$	$\text{cal gfw}^{-1}$	$^{\circ}\text{K}$	$\text{cal gfw}^{-1}$
$\alpha \rightarrow \beta$	$823 \pm 3$	220	823	110
$\beta \rightarrow \gamma$	$1061 \pm 5$	260	1061	220

Magnesium nitride does not melt but decomposes on heating, and the decomposition temperatures reported differ considerably. Brewer *et al*<sup>6</sup> reported  $1300^{\circ}\text{K}$ , while Zhukov<sup>7</sup> and Hagg<sup>8</sup> report that decomposition does not occur after heating the compound to  $1523^{\circ}$  and  $1276^{\circ}\text{K}$ , respectively. Others, such as Lipski,<sup>9</sup> Fichter and Scholly,<sup>10</sup> and Lafitte *et al*,<sup>11</sup> also report that this compound decomposes but show wide discrepancies in the data. Mitchell<sup>3</sup> has estimated the decomposition temperature to be  $1790^{\circ}\text{K}$  by calculating the free energy from an estimated entropy but, also, urges caution in its acceptance because of the large error made in the  $\gamma$ -phase heat capacity. Since none of the reported values agree, these tables have been calculated by extrapolating the  $\gamma$  phase to an arbitrary temperature of  $2500^{\circ}\text{K}$ .

#### b. Thermodynamic Properties

##### 1) Heat-capacity and enthalpy relations

Sato<sup>5</sup> derived a heat-capacity equation over the range  $0^{\circ}$  to  $418.2^{\circ}\text{C}$  ( $273.3^{\circ}$  to  $691.5^{\circ}\text{K}$ ), but Mitchell<sup>3</sup> made enthalpy measurements to  $1272.5^{\circ}\text{K}$  and reported two transitions within that range. From these data, he derived three heat-capacity equations, and they have been used in the calculations of these tables. The uncertainty in the heat capacity used for the calculation of the Table of Uncertainties is the difference between the heat capacity calculated by the Kelley<sup>4</sup> and the Mitchell<sup>3</sup> relationships for each phase.



## 2) Standard heat of formation

A wide variation occurs in the literature for the  $\Delta H_f^{\circ}$  value of this compound; it has been determined by direct and indirect methods. Neumann *et al*<sup>12,13</sup> nitrated magnesium in the presence of an oxide catalyst and obtained a value of  $-116 \pm 2$  kcal gfw<sup>-1</sup> and, then, used an indirect solution method to get a value of  $-113.9$  kcal gfw<sup>-1</sup>.

Brunner<sup>14</sup> hydrolyzed the compound to obtain a value of  $-114.9$  kcal gfw<sup>-1</sup>. Matignon<sup>15</sup> used a solution method and obtained a value of  $-134.3$  kcal gfw<sup>-1</sup>. These data have been recalculated by Bichowsky and Rossini<sup>16</sup> to yield  $-137$  kcal gfw<sup>-1</sup>. Mitchell,<sup>3</sup> also, used the hydrolysis in dilute HCl and reported a value of  $-110.24 \pm 0.275$  kcal gfw<sup>-1</sup>. This value has been used in the calculation of these tables because of the reported purity of the starting product and the treatment of the data.

## 3) Entropy

Mitchell<sup>3</sup> calculated the entropy of magnesium nitride to be  $22.4$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> by using a modified form of Latimer's Rule for estimating the entropy of oxides. Brewer *et al*<sup>6</sup> reported the standard entropy of formation of this compound as  $-47.2$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>, which yields a value of  $21.97$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> as the entropy when calculated by using the corresponding entropies of the elements reported in these tables.<sup>17\*</sup> Mitchell's value of  $22.4$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> has been used here.

## 4) Vaporization data

It is generally considered that Mg<sub>3</sub>N<sub>2</sub> vaporizes to form gaseous magnesium and nitrogen. The works of Zhukov,<sup>7</sup> Hagg,<sup>8</sup> Lipski,<sup>9</sup> Fichter and Scholly,<sup>10</sup> and Lafitte, Elchardus, and Grandadam<sup>11</sup> have already been mentioned as giving somewhat different behavior on heating. The more recent work of Soulen, Sthapitanonda, and Margrave<sup>18</sup> gives details of effusion studies from Mg<sub>3</sub>N<sub>2</sub>. They conclude that Mg<sub>3</sub>N<sub>2</sub> may vaporize by a complex mechanism with the final equilibrium products being Mg(g) and N<sub>2</sub>(g). Their data for small effusion holes approached that calculated by Third-Law methods, using data similar to that accepted in the present tabulation.

\*The tables referred to for elemental Mg and O<sub>2</sub> are also found in volume 2 of this compilation.

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## 12.4 Magnesium Oxide

Detailed analyses were made for  $\text{MgO}_{(s,l)}$  and  $\text{MgO}_{(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

### 12.4.1 Magnesium Oxide ( $\text{MgO}_{(s,l)}$ , $\text{MgO}_{(g)}$ )

#### a. Condensed Phase

The melting point of magnesium oxide was measured and reported by McNally, Peters, and Ribbe<sup>1</sup> to be  $3098^\circ \pm 20^\circ\text{K}$ .

The value of  $\Delta H_{f298}^\circ$  for solid  $\text{MgO}$  reported by Holley and Huber,<sup>2</sup> -143.7 kcal/gfw, was adopted herein. This value, obtained by combustion calorimetry, was in excellent agreement with the value of -143.84 kcal/gfw determined by Shomate and Huffman<sup>3</sup> from the heat of solution of  $\text{MgO}$  in  $\text{HCl}$ . Moose and Paar<sup>4</sup> had earlier reported the value -146.1 kcal/gfw for this heat of formation. No weight was given to this last value in assigning an uncertainty of  $\pm 0.5$  kcal/gfw.

The table of thermodynamic functions for the condensed phases of  $\text{MgO}$  was revised to incorporate the new melting point, maintaining the heat of fusion as 18.5 kcal/gfw. Other properties previously reported<sup>5</sup> were retained.

#### b. Gaseous Magnesium Oxide

As previously noted,<sup>5</sup> it was not certain that the lowest state of the singlet systems of  $\text{MgO}_{(g)}$  was the ground state of the molecule. As a matter of fact, the best evidence was to the contrary. The previous table of the thermodynamic functions of  $\text{MgO}_{(g)}$ ,<sup>5</sup> which adopted a  $^1\Sigma$  ground state was replaced by the result of a new calculation based on a  $^3\Sigma$  ground state.

Brewer and Porter<sup>6</sup> observed several ultraviolet systems for  $\text{MgO}_{(g)}$  which they interpreted as evidence for adjacent  $^3\Sigma$  and  $^3\Pi$  states lying  $55 \pm 15$  kcal/gfw below the lowest  $^1\Sigma$  state. It had been shown<sup>7-9</sup> that parts of their systems were probably due to  $\text{MgOH}$  and polymers containing  $\text{Mg}$  and  $\text{O}$ . Thrush<sup>10</sup> had recently reported, however, that only Brewer and Porter's system-I was observed in absorption, and that this spectrum was unaffected by the addition of water.

In the revised calculations of the thermodynamic functions of  $\text{MgO}_{(g)}$  reported herein, Brewer and Porter's<sup>6</sup> vibration analysis of their system-I (taken to be due to transitions between  $^3\Sigma$  states) was adopted. The low-lying  $^1\Sigma$  state was taken to be 55 kcal/gfw ( $19,200\text{ cm}^{-1}$ ) above the  $^3\Sigma$  ground state. Bulewicz and Sugden<sup>9</sup> reported this interval to be 45 kcal/gfw. Values of  $B_e$  for the triplet states were estimated from an average  $B_e/\omega_e$  ratio of analyzed singlet states. The spectroscopic constants used for the revised calculation of the thermodynamic functions were (in units of  $\text{cm}^{-1}$ ) as follows:

TABLE 34  
SPECTROSCOPIC CONSTANTS FOR MgO(g)

State	E	(cm <sup>-1</sup> )				
		$\omega_e$	$\omega_e x_e$	$B_e$	$a_e$	$D_e (\times 10^6)$
$\chi \ ^3\Sigma$	0	902	13.0	0.625	0.009	1.2
$\ ^3\Sigma$	26863.9	817	9.5	0.585	0.008	1.2
$\chi' \ ^1\Sigma$	19200.	782.84	5.15	0.5711	0.005	1.22
$A \ ^1\pi$	22694.4	664.4	3.91	0.5056	0.0046	1.2
$B \ ^1\Sigma$	39204.7	824.1	4.76	0.5822	0.0045	1.2

Dissociation energy values at 0°K for MgO(g) ranging from 85 to 120 kcal/gfw had been reported. The spread of values was due in part to different assumptions as to the ground state of the molecule and, in part, to experimental difficulties in determining relative amounts of dissociated and undissociated vaporizing species. A Birge-Spencer extrapolation of the singlet system gave 85 kcal/gfw for  $D_0^\circ$ . Porter, Chupka, and Inghram<sup>11</sup> reported  $D_0^\circ$  to be less than 90 kcal/gfw ( $^3\Sigma$  ground state) from mass spectrometric studies in which vaporization was due to the gaseous elements at 1950°K. However, it was possible that the experimental arrangement actually provided reducing conditions.<sup>12</sup>

From flame studies, Huldt and Lagerqvist<sup>13</sup> reported  $D_0^\circ$  to be 120 kcal/gfw ( $^1\Sigma$  ground state), a value which was recalculated to 115 kcal/gfw ( $^3\Sigma$  ground state) by Brewer and Porter.<sup>6</sup> From vapor-pressure measurements, Brewer and Porter<sup>6</sup> reported a heat of sublimation at 298.15°K of 130 kcal/gfw, which corresponded to a  $D_0^\circ$  of 108 kcal/gfw ( $^3\Sigma$  ground state). Flame-photometry studies of Bulewicz and Sugden<sup>9</sup> gave  $98 \pm 2$  kcal/gfw ( $^3\Sigma$  ground state) for  $D_0^\circ$ . Veits and Gurvich,<sup>14, 15</sup> using a flame technique, reported  $D_0^\circ$  to be 100 kcal/gfw. Gaydon<sup>16</sup> recommended a value of  $104 \pm 16$  kcal/gfw for this quantity.

For the present compilation,  $D_0^\circ$  was taken to be 105 kcal/gfw, which corresponded to a  $\Delta H_{298}^\circ$  for MgO(g) of -11.1 kcal/gfw. An uncertainty of  $\pm 15$  kcal/gfw was assigned to  $\Delta H_{298}^\circ$ .

The vaporization temperature of MgO, the temperature at which the sum of the partial pressures of all vaporizing species equals 1 atm has been calculated. The assumption has been made that vaporization by dissociation produces equilibrium amounts of O and O<sub>2</sub>. The vaporization temperature so calculated is 3110°K, which is very near the melting point. It has been calculated that the principal vaporizing species is undissociated MgO(g). Required data have not been available for an estimate of contributions of possible polymeric species. Mott<sup>17</sup> has reported the boiling point of MgO to be 3900°K.

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### 13. Manganese Compounds

The only manganese compounds investigated in this study were the oxides.

#### 13.1 Manganese Borides

The borides of manganese were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 13.2 Manganese Carbides

The carbides of manganese were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 13.3 Manganese Nitrides

The nitrides of manganese were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 13.4 Manganese Oxides

A detailed analysis was made for  $\text{MnO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

##### 13.4.1 Manganese Oxide ( $\text{MnO}_{(g)}$ )

The spectroscopic constants used for the calculation of the thermodynamic functions of  $\text{MnO}_{(g)}$  were (in units of  $\text{cm}^{-1}$ ) as follows:

E	$\omega_e$	$\omega_e x_e$	$\omega_e y_e$	$B_e$	$D_e (\times 10^7)$
0	839.55	4.79	---	0.499	7.1
17909.59	762.75	9.60	0.06	0.453	6.4

The vibrational constants for the two electronic states were from Das Sarma,<sup>1</sup> who modified the constants reported by Herzberg<sup>2</sup> for the same two states. Das Sarma calculated a dissociation energy at 0°K of 95 kcal/gfw for the lower state by a Birge-Sponer linear extrapolation of his data. From volatility studies on MnO, Brewer and Mastick<sup>3</sup> concluded that  $D_0$  was less than 106 kcal/gfw. From flame studies, Huldt and Lagerqvist<sup>4</sup> reported  $D_0$  to be  $92 \pm 9$  kcal/gfw. Because of the agreement between the thermochemical and spectroscopic values of  $D_0$ , the lower of the two electronic states was taken to be the ground state of  $\text{MnO}_{(g)}$ .

A rotational analysis of the states had not been made. The internuclear distance of the ground state was estimated to be  $1.65\text{\AA}$  corresponding to a value of  $0.499\text{ cm}^{-1}$  for  $B_e$ . The internuclear distance for the ground state was estimated to be  $1.67\text{\AA}$  by Brewer and Chandrasekharaiah<sup>5</sup> and  $1.79\text{\AA}$  by Das Sarma.<sup>1</sup>  $B_e$  for the upper electronic state was estimated to be  $0.453\text{ cm}^{-1}$  from the assumption that  $\omega_e/B_e$  would be a constant ratio for the various electronic states of a given molecule. Values of  $D_e$  were estimated from the relation  $D_e = 4B_e^3/\omega_e^2$ . The statistical weights of the ground and excited electronic states were assumed to be 4 and 2, respectively.

$D_0^\circ$  for  $\text{MnO(g)}$  was taken to be 95 kcal/gfw from Das Sarma.<sup>1</sup> With appropriate thermodynamic functions from the present compilation,  $\Delta H_{f298}^\circ$  was calculated to be 30.600 kcal/gfw. An uncertainty of  $\pm 10.000$  kcal/gfw was assigned to this quantity.

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## 14. Molybdenum Compounds

The only molybdenum compounds investigated in this study were the carbides and oxides.

### 14.1 Molybdenum Borides

The borides of molybdenum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 14.2 Molybdenum Carbides

In this study, detailed analyses of molybdenum carbides were made for  $\text{Mo}_2\text{C}_{(s)}$  and  $\text{Mo}_3\text{C}_{2(s)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 14.2.1 Dimolybdenum Carbide ( $\text{Mo}_2\text{C}_{(s)}$ )

##### a. Phase Diagram, Crystal Structure, Melting Point

The data on the molybdenum-carbon phase system have been reviewed by Hansen,<sup>1</sup> Schwarzkopf and Kieffer,<sup>2</sup> and more recently by Storms.<sup>3</sup> The existence of two intermediate phases in this system has been established. The lower carbide has an integral stoichiometry of  $\text{Mo}_2\text{C}$  with a homogeneity range between  $\text{MoC}_{0.44}$  and  $\text{MoC}_{0.51}$  at about  $1400^\circ\text{C}$ .<sup>4, 5, 6, 12</sup>

The crystal structure of  $\text{Mo}_2\text{C}$  was first determined by Westgren and Phragmen<sup>6</sup> who found an hexagonal close-packed structure. Since then, many investigators have determined the lattice parameters.<sup>1</sup> The lattice parameters given in Hansen,<sup>1</sup>  $a = 3.002 \text{ \AA}$  and  $c = 4.724 \text{ \AA}$ , are those determined by Kuo and Hägg,<sup>7</sup> who prepared this  $\text{Mo}_2\text{C}$  by carburizing Mo with CO. (Nowotny, Parthe, Kieffer, and Benesovsky<sup>8</sup> have suggested such samples may be contaminated with oxygen.) Fries and Kempter<sup>9</sup> performed X-ray studies on sintered pellets which had been prepared by pressing  $\text{Mo}_2\text{C}$  powder. They report an hexagonal structure with  $a = 3.003 \text{ \AA}$  and  $c = 4.729 \text{ \AA}$ . Rudy, Benesovsky, and Sedlatschek<sup>10</sup> obtained measurements of the lattice parameters of the  $\text{Mo}_2\text{C}$  phase on both sides of the single-phase region. On the Mo-rich side they obtained  $a = 2.997$  and  $c = 4.727 \text{ \AA}$ , and for  $\text{Mo}_2\text{C}$  in equilibrium with  $\text{Mo}_3\text{C}_2$  they obtained  $a = 3.012$  and  $c = 4.736 \text{ \AA}$ . They determined the structure to be an hexagonal  $\text{I}1\bar{3}$ -type. In some very recent work,



Wallace, Gutierrez, and Stone<sup>12</sup> determined the variation of lattice parameters with composition across the  $\text{Mo}_2\text{C}$  single-phase region at  $2100^\circ\text{C}$ . For  $\text{Mo}_2\text{C}$  in equilibrium with  $\alpha\text{-Mo}$ , they report  $a = 2.994$  and  $c = 4.722 \text{ \AA}$ . They obtained  $a = 3.015 \text{ \AA}$  and  $c = 4.739 \text{ \AA}$  for lattice parameters when  $\text{Mo}_2\text{C}$  was in equilibrium with  $\text{Mo}_3\text{C}_2$ . Lauder and Germer<sup>11</sup> found evidence for a face-centered cubic form with  $a = 4.15 \text{ \AA}$ . This structure has not been subsequently substantiated.

The phase diagram given by Hansen<sup>1</sup> was constructed by Nowotny and co-workers and is based on an earlier diagram given by Sykes et al.<sup>4</sup> The  $\text{Mo}_2\text{C}$  phase was shown to melt peritectically at about  $2400^\circ\text{C}$ . Other reported melting temperatures of  $\text{Mo}_2\text{C}$  given by Hansen are  $2280 \pm 50^\circ\text{C}$ ,  $2690 \pm 50^\circ\text{C}$  and  $2405^\circ\text{C}$ . More recently, Nadler and Kempter<sup>13</sup> determined the melting temperature of  $\text{Mo}_2\text{C}$  to be  $2410 \pm 15^\circ\text{C}$ . In a study of melting temperature as a function of composition, Wallace et al.<sup>12</sup> determined that the  $\text{Mo}_2\text{C}$  phase melts peritectically at  $2440 \pm 30^\circ\text{C}$ . In this compilation, the melting temperature is taken as  $2420^\circ\text{C}$ .

The phase relations are not completely understood in the composition range of 35 to 100 atom-percent carbon. Although some structure data and melting points were reported for the higher carbide earlier, the first liquidus curves were determined by Nowotny and co-workers.<sup>8</sup> They reported a maximum in the liquidus curve of  $2650^\circ\text{C}$  at a composition close to  $\text{MoC}$ , and they found an eutectic at about 70 atom-percent C and approximately  $2400^\circ\text{C}$ . Also, they found that  $\text{MoC}$  disproportionates upon cooling to  $\text{Mo}_2\text{C}$  and C somewhere between  $1900$  and  $700^\circ\text{C}$ . They also determined the crystal structure which will be discussed later.

In sharp disagreement with these results is the work of Wallace<sup>12</sup> and co-workers who determined lattice parameters and melting temperatures for a number of alloys with compositions between 25 and 50 atom-percent C. From X-ray and chemical analysis of samples annealed at  $2100^\circ\text{C}$ , these investigators found the composition of the higher carbide to be  $38.2 \pm 0.5$  atom-percent C. Similar analysis of arc-melted samples with 43 to 50 atom-percent C showed the composition of the carbide phase to be  $40.8 \pm 0.5$  atom-percent C. With increasing temperatures, therefore, the carbon-rich phase boundary appears to move toward higher carbon content. The homogeneity range of the single-phase region is apparently narrow, since they found samples containing 37 atom-percent C contained  $\text{Mo}_2\text{C}$ .

Thus, according to the results of Wallace et al, the integral stoichiometry of the higher carbide is  $\text{Mo}_3\text{C}_2$  rather than  $\text{MoC}$ . Wallace and co-workers also determined the melting temperatures of a number of alloys with compositions between 34 and 51 atom-percent C. Chemical analysis of a sample containing 37 atom-percent C showed no free carbon present, and a melting temperature of  $2460^\circ\text{C}$  was determined. This is in agreement with the previously determined  $\text{Mo}_2\text{C}$  peritectic. Analysis of a sample containing 38 atom-percent C revealed no free carbon, but a melting temperature of  $2590^\circ\text{C}$  was determined. Samples with compositions of 41 to 51 atom-percent C all contained free carbon, and the melting temperatures were  $2570$  to  $2580^\circ\text{C}$ . Since the method of determining melting temperatures used by Wallace et al<sup>12</sup> was that of observing when the blackbody hole filled with liquid as the temperature was being raised, and since the  $\text{Mo}_3\text{C}_2$  homogeneity range is apparently narrow, the melting temperature of  $2580 \pm 30^\circ\text{C}$  which they report for the composition range 38 to 51 atom-percent C would presumably be the  $\text{Mo}_3\text{C}_2$  - C eutectic temperature. They did not find a maximum at 50 atom-percent carbon. There are two possible explanations for the fact that they did not find a maximum in the vicinity of 38 atom percent C which one would expect for the  $\text{Mo}_3\text{C}_2$  single-phase region. The composition of the sample reported to contain 38 atom-percent C may have been slightly different so that in fact its composition was in the  $\text{Mo}_3\text{C}_2$  - C two-phase region, or the melting temperature of the single phase may be only slightly higher than the  $\text{Mo}_3\text{C}_2$  eutectic temperature.

These data are in disagreement with those of Nowotny et al<sup>8</sup> who reported a maximum melting temperature of  $2650^\circ\text{C}$  at 50 atom-percent C, and an  $\text{MoC}$ -C eutectic temperature of about  $2400^\circ\text{C}$ . Clearly, however, if the temperature and overall composition determinations by Wallace et al,<sup>12</sup> are correct, Nowotny's phase diagram is in error. Even if Wallace and co-workers had failed to correctly determine the amount of free carbon in their samples, for samples of overall composition 38 to 51 atom-percent C they should have determined a melting temperature of about  $2400^\circ\text{C}$  (the  $\text{Mo}_2\text{C}$  peritectic) if Nowotny's phase diagram were correct. Furthermore, the detection of the hexagonal higher carbide by X-ray diffraction at overall composition of 38 atom-percent carbon is convincing evidence that the composition of this phase lies at about 38 atom-percent C.

The best interpretation of the data would appear to be that the higher carbide has a composition of about 38 atom-percent C at  $2100^\circ\text{C}$ , which corresponds to an integral stoichiometry of  $\text{Mo}_3\text{C}_2$ . The  $\text{Mo}_3\text{C}_2$ -C eutectic temperature is  $2580 \pm 30^\circ\text{C}$  and the melting temperature of the  $\text{Mo}_3\text{C}_2$  single phase is approximately  $2650^\circ\text{C}$  ( $2923^\circ\text{K}$ ). Below  $1450^\circ\text{C}$ ,  $\text{Mo}_3\text{C}_2$  decomposes to  $\text{Mo}_2\text{C}$  and C.<sup>12</sup>

A number of investigators have attempted to determine the crystal structure of  $\text{Mo}_3\text{C}_2$ . Most of these are summarized in Hansen.<sup>1</sup> Kuo and Hägg<sup>7</sup> reported an hexagonal  $\gamma$ -phase (WC-type) with  $a = 2.898\text{\AA}$  and  $c = 2.809$  formed by high-temperature carburization of Mo with CO. Below  $800^\circ\text{C}$ , this reaction yielded a  $\gamma'$ -phase with  $a = 2.932$  and  $c = 10.97\text{\AA}$ . Nowotny and co-workers<sup>8</sup> were the first to solve the complex structure. They found an hexagonal structure with  $a = 3.00$  and  $c = 14.61\text{\AA}$ . Also, in arc-melted samples they found a face-centered cubic phase with  $a = 4.26\text{\AA}$ . They believe that a high-temperature cubic modification may exist. They also suggested the samples of Kuo and Hägg may have been contaminated with oxygen. Rudy and co-workers<sup>10</sup> also determined the structure and found  $a = 3.013$  and  $c = 14.64\text{\AA}$  in good agreement with Nowotny *et al.*<sup>8</sup> Rudy and co-workers also were first to determine that the composition of the higher carbide lies at about 40 atom-percent C rather than at 50 atom-percent. Wallace and co-workers<sup>12</sup> found  $a = 3.01$  and  $c = 14.61\text{\AA}$  with no detectable variation in lattice parameters with composition. The space group is  $D_{6h}^4$ .

## b. Thermodynamic Properties

### 1) Heat capacity and entropy at $298^\circ\text{K}$

There are no low-temperature heat capacity data available for the  $\text{Mo}_2\text{C}$  phase, and thus the entropy at  $298^\circ\text{K}$  is unknown. By comparing  $\Delta S$  for the reaction,  $x\text{M} + y\text{C} = \text{M}_x\text{C}_y$  for a number of transition metal carbides, Krikorian<sup>14</sup> has estimated the entropy of  $\text{Mo}_2\text{C}$  at  $298^\circ\text{K}$  to be  $17.1 \pm 1.0 \text{ e.u.}$  This value is used in the preparation of the tables.

### 2) High-temperature heat capacity

No high-temperature heat-content measurements have been made for  $\text{Mo}_2\text{C}$ . By considering the known high-temperature heat capacities, the known entropies at  $298^\circ\text{K}$ , and the stoichiometry of a number of transition metal carbides, Krikorian<sup>15</sup> has derived an equation for estimating the heat capacities of carbides. The equation derived by Krikorian is

$$\frac{2 C_p^o}{x+y} = 6.74 + 0.582 S_{298}^o \left( \frac{2}{x+y} \right) + \left[ 2.93 \times 10^{-3} - 0.92 \times 10^{-4} S_{298}^o \left( \frac{2}{x+y} \right) \right] T + \left[ -3.65 \times 10^5 + 1.02 \times 10^4 S_{298}^o \left( \frac{2}{x+y} \right) \right] T^{-2},$$

where  $C_p$  is the heat capacity in cal degK<sup>-1</sup>gfw<sup>-1</sup>, and x and y refer to a carbide of the formula  $M_xC_y$ .

From equilibrium measurements, Gleiser and Chipman<sup>16</sup> determined the free energy of formation of  $Mo_2C$ . A second law treatment of the data yielded the heat of formation of  $Mo_2C$  at 1270°K from which a value for  $\Delta S_{1270}^o$  of 1.83 e.u. was calculated. These data are discussed in the next section. This value for  $S_{1270}^o$  has been combined with the entropies for Mo and C given by Barriault et al<sup>17</sup> to obtain  $S_{1270}^o = 40.93$  e.u. for  $Mo_2C$ .\*

Since these are the only data available with which to compare the estimated  $C_p$  equation, the constant term of the equation was adjusted slightly so that the calculated entropy at 1270°K would agree with Gleiser and Chipman's value.

The resulting equation for the high-temperature heat capacity of  $Mo_2C$  is

$$C_p^o = 15.92 + 2.82 \times 10^{-3} T - 3.74 \times 10^5 T^{-2}.$$

This equation is used in the preparation of the  $Mo_2C$  table.

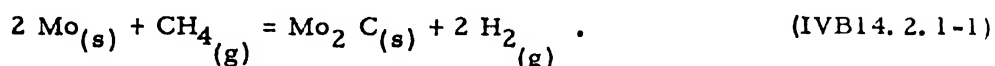
### 3) Heat of formation

No calorimetric determinations of the heat of formation of  $Mo_2C$  have been reported. Kelley<sup>18</sup> reported free energy values for  $Mo_2C$  based on the equilibrium data of Schenck, Karzer, and Wesselcock<sup>19</sup> who studied the  $Mo - Cl_4 - H_2 - Mo_2C$  system. These investigators used a static system in which thermal segregation of gases must have occurred. For samples which contained more than

\* The entropies for Mo and C referred to are tabulated in volume 2 of this compilation.

about 6 wt. percent C, the measured  $H_2/CH_4$  ratio at equilibrium was somewhat less than that for the  $C-H_2 - CH_4$  system. Furthermore, the results of their measurements on  $C-H_2 - CH_4$  equilibrium by the same method are not in agreement with the presently accepted data on this system.

More recently, Browning and Emmett<sup>20</sup> have investigated the same system over the temperature range 720 to 952°K using a dynamic method. They analyzed the gas stream for  $H_2$ , took the  $CH_4$  by difference, and from the known total pressure in the system calculated the equilibrium constant for the reaction



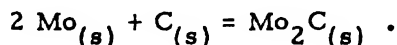
They then plotted  $\log K_{eq}$  versus  $1/T$  and drew a straight line through the somewhat scattered points. Over this temperature range, this straight line plot is fitted by the equation

$$\Delta F_T^0 = + 36,420 - 51.1 T.$$

The entropy change of 51.1 e.u. for reaction (IVB14. 2. 1-1) is unreasonably large. The currently accepted values for the heat and entropy of formation of methane at 900°K are -21,210 cal gfw<sup>-1</sup> and -25.8 e. u., respectively. If these values are combined with the above equation (IVB14. 2. 1-1) at the 900°K, the equation

$$\Delta F_T^0 = + 15,210 - 25.3 T$$

is obtained for the free energy at 900°K for



Clearly, an entropy change of 25.3 e.u. is unreasonable.

If one uses estimated entropies for  $\text{Mo}_2\text{C}$ , a third-law calculation can be carried out for each of Browning and Emmett's experimental points. For these calculations,  $\Delta S_f^\circ$  of  $\text{Mo}_2\text{C}$  was assumed to be 1.8 e.u. and independent of temperature over the temperature range of interest. The entropies of  $\text{CH}_4$  and  $\text{H}_2$  were taken from the JANAF tables.<sup>21</sup> The heats for reaction (IVB14. 2. 1-1) calculated by this method decreased with increasing temperature from  $\Delta H^\circ = +17,600 \text{ cal gfw}^{-1}$  at  $785^\circ\text{K}$  to  $\Delta H^\circ = 14,220 \text{ cal gfw}^{-1}$  at  $952^\circ\text{K}$ . Since  $\Delta C_p^\circ$  for reaction (IVB14. 2. 1-1) is only about  $2 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ , a difference of less than  $400 \text{ cal gfw}^{-1}$  in the heats would be expected. One therefore concludes that the determinations of Browning and Emmett are not especially reliable.

The most reliable available data appear to be the determinations of the partial pressures of  $\text{CO}$  and  $\text{CO}_2$  above the  $\text{Mo} - \text{Mo}_2\text{C} - \text{MoO}_2$  system by Gleiser and Chipman.<sup>16</sup> These investigators determined the partial pressures over the temperature range  $1200$  to  $1340^\circ\text{K}$ , and from the known thermodynamic properties of  $\text{MoO}_3$ ,  $\text{CO}$ , and  $\text{CO}_2$ , they calculated the free energy of formation of  $\text{Mo}_2\text{C}$ . They found that a plot of  $\Delta F_f^\circ$  of  $\text{Mo}_2\text{C}$  versus  $1/T$  could be expressed by the equation

$$\Delta F_f^\circ = -11,710 - 1.83 T$$

over the temperature range  $1200$  to  $1340^\circ\text{K}$ . In the same work, those investigators determined the free energy of formation of  $\text{MoO}_2$ , from which they calculated  $\Delta H_{f298}^\circ$  to be  $-141.5 \text{ kcal gfw}^{-1}$ . The agreement between this value and the calorimetric value of  $-140.8 \text{ kcal gfw}^{-1}$  gives some confidence in their determinations for  $\text{Mo}_2\text{C}$ . Consequently,  $-11,710 \text{ cal gfw}^{-1}$  has been adopted for the heat of formation of  $\text{Mo}_2\text{C}$  at  $1270^\circ\text{K}$ .

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#### 14.2.2 Trimolybdenum Dicarbide ( $\text{Mo}_3\text{C}_2(\text{s})$ )

##### a. Phase Diagram, Crystal Structure, and Melting Point

In the discussion of the  $\text{Mo}_2\text{C}$  phase, the phase data for the entire Mo-C system are discussed. The composition of the  $\text{Mo}_3\text{C}_2$  phase has been shown by Rudy and co-workers<sup>1</sup> and by Wallace and co-workers<sup>2</sup> to lie at  $38.2 \pm 0.5$  atom-percent C at  $2100^\circ\text{C}$ . These results are in disagreement with the phase data of Nowotny *et al*<sup>3</sup> who reported the maximum melting temperature occurred for an alloy containing 50 atomic percent C. The homogeneity range of the  $\text{Mo}_3\text{C}_2$  phase is apparently quite narrow at  $2100^\circ\text{C}$ . The melting temperature of this phase is approximately  $2650^\circ\text{C}$  ( $2923^\circ\text{K}$ )<sup>3</sup>, and below about  $1450^\circ\text{C}$   $\text{Mo}_3\text{C}_2$  disproportionates into  $\text{Mo}_2\text{C}$  and C.<sup>2</sup> In this report,  $1700^\circ\text{K}$  has been taken as the disproportionation temperature of the  $\text{Mo}_3\text{C}_2$  phase.

##### b. Thermodynamic Properties

###### 1) Heat capacity and entropy at $298.15^\circ\text{K}$

No low-temperature heat capacity measurements have been made on  $\text{Mo}_3\text{C}_2$ , and thus the entropy at  $298^\circ\text{K}$  is unknown. By comparing  $\Delta S^\circ$  for the reaction  $x\text{M} + y\text{C} = \text{M}_x\text{C}_y$  for a number of transition metal carbides, we have estimated  $\Delta S^\circ_{298}$  for formation of  $\text{Mo}_3\text{C}_2$  as  $+0.50$  e. u. From the entropies of molybdenum and carbon given in the compilation by Barriault *et al*<sup>4</sup> an entropy at  $298.15^\circ\text{K}$  of  $+23.7$  e. u. was obtained for  $\text{Mo}_3\text{C}_2$ . This value is used in the preparation of the tables.

###### 2) High-temperature heat capacity

There have been no high-temperature heat-content measurements reported for  $\text{Mo}_3\text{C}_2$ . The equation, given by Krikorian<sup>5</sup> which is discussed in the section on  $\text{Mo}_2\text{C}$  in this report, has been used to obtain estimated high-temperature heat capacities for  $\text{Mo}_3\text{C}_2$ . The resulting equation is

$$C_p^\circ = 30.65 + 5.144 \times 10^{-3} T - 6.707 \times 10^{-5} T^2$$

in which  $C_p^\circ$  is the heat capacity in  $\text{cal deg K}^{-1} \text{ gfw}^{-1}$ .

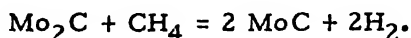
###### 3) Heat of formation

There have been no calorimetric determinations of the heat of formation of  $\text{Mo}_3\text{C}_2$ , but several authors have reported values for free energy of formation from equilibrium measurements.

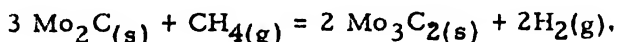
\*The tables referred to for Mo and C have also been compiled in volume 2 of this work for convenience.



Browning and Emmett<sup>6</sup> performed some equilibrium experiments on a system which was thought to contain  $\text{Mo}_2\text{C}$ , "MoC",  $\text{CH}_4$  and  $\text{H}_2$ . From the pressures of  $\text{CH}_4$  and  $\text{H}_2$  in the system, they calculated the equilibrium constant for the reaction



At the time these experiments were carried out, the higher carbide was assumed to have an integral stoichiometry of MoC. The sample which Browning and Emmett used in this investigation contained approximately 40 atom-percent C, which happens to correspond to an integral stoichiometry of  $\text{Mo}_3\text{C}_2$ . Furthermore, the presence of MoC in the sample was deduced from an X-ray pattern which showed lines that agreed with the hexagonal  $\gamma$ -phase (WC-type) reported by Kuo and Hägg<sup>7</sup>. The lattice parameters for this structure were reported by Kuo and Hägg to be  $a = 2.898\text{\AA}$  and  $c = 2.809\text{\AA}$ . As is pointed out in the discussion on the  $\text{Mo}_2\text{C}$  phase, however, this structure is not now regarded as the correct one for  $\text{Mo}_3\text{C}_2$ . The sample was prepared by carburization of Mo with CO at  $680^\circ\text{C}$ . The equilibrium measurements with  $\text{CH}_4$  and  $\text{H}_2$  were carried out at about  $800^\circ\text{C}$ . The work of Wallace *et al*<sup>2</sup> indicates  $\text{Mo}_3\text{C}_2$  is unstable with respect to  $\text{Mo}_2\text{C}$  and C below  $1450^\circ\text{C}$ . The solid phases which were actually present in the investigations of Browning and Emmett<sup>6</sup> are thus not well established. If one supposes that Browning and Emmett were in fact studying the equilibrium



a second-law treatment of their data yields a value for  $\Delta S^\circ$  for this reaction of -21.3 e.u. This value is clearly unreasonable since an entropy change of about +20 e.u. would be expected. For these reasons the data of Browning and Emmett have not been used in preparation of these tables.

By means of equilibrium measurements between  $\text{MoC}_{1-x}$  and  $\text{NbC}_{1-x}$  ( $x \approx 0.25$ ), Rudy<sup>1</sup> found that at  $1850^\circ\text{C}$

$$\Delta F_f^\circ (\text{MoC}_{1-x}) - \Delta F_f^\circ (\text{NbC}_{1-x}) \approx 19 \text{ to } 22 \text{ kcal gfw}^{-1}$$

He used a value of  $-28 \text{ kcal/gfw}$ <sup>8</sup> for the free energy of formation of  $\text{NbC}_{1-x}$  and thus obtained:

$$\Delta F_f^\circ (\text{MoC}_{1-x}) = -6 \text{ to } -9 \text{ kcal gfw}^{-1}.$$

Wallace<sup>2</sup> has claimed that the value of  $-28 \text{ kcal gfw}^{-1}$  used by Rudy for the free energy of formation of  $\text{NbC}_{1-x}$  is the value one would expect for  $\text{NbC}_{1.0}$ . He calculated a value of  $-23 \text{ kcal gfw}^{-1}$  for the free energy of formation of  $\text{NbC}_{0.75}$ , which changes Rudy's results to

$$\Delta F_f^\circ (\text{MoC}_{1-x}) = -1 \text{ to } -4 \text{ kcal gfw}^{-1}.$$

Wallace and co-workers<sup>2</sup> carried out similar measurements at  $2100^\circ\text{C}$  in the  $\text{MoC}_{0.61}$ - $\text{ZrC}_{0.92}$  equilibrium region.

They found

$$\Delta F_f^\circ (\text{MoC}_{0.61}) - \Delta F_f^\circ (\text{ZrC}_{0.92}) = 35.8 \text{ kcal gfw}^{-1}.$$

From the thermodynamic data given in the JANAF tables<sup>9</sup> for  $\text{ZrC}_{1.0}$ , they calculated

$$\begin{aligned} \Delta F_f^\circ (\text{ZrC}_{1.0}) &= -40.3 < \Delta F_f^\circ (\text{ZrC}_{0.92}) < -36.4 \text{ kcal gfw}^{-1} \\ &= 0.92 \Delta H_f^\circ (\text{ZrC}_{1.0}) - T \Delta S^\circ, \end{aligned}$$

and thus obtained

$$\Delta F_f^\circ (\text{MoC}_{0.61}) = -0.6 \text{ to } -4.5 \text{ kcal gfw}^{-1}.$$

The free energies of formation of  $\text{NbC}_{0.75}$  and  $\text{ZrC}_{0.92}$  have been recalculated using the free energies of formation of  $\text{NbC}_{1.0}$  and  $\text{ZrC}_{1.0}$  given in the present compilation made herein.  $\text{NbC}_{0.75}$  was treated as a solution of 0.75 mole of  $\text{NbC}_{1.0}$  in 0.25 mole of Nb, and  $\text{ZrC}_{0.92}$  was regarded as a solution of 0.92 mole of  $\text{ZrC}_{1.0}$  in 0.08 mole of Zr. Raoult's Law was then assumed, and the activities of the components were taken equal to their respective mole fractions. A summary of the quantities used in these calculations is listed below with the results:

$$\Delta F_f^\circ_{2100^\circ\text{K}} (\text{NbC}_{1.0}) = -32.2 \pm 2.0 \text{ kcal gfw}^{-1}$$

$$\Delta F_f^\circ_{2100^\circ\text{K}} (\text{NbC}_{0.75}) = -26.5 \pm 2.0 \text{ kcal gfw}^{-1}$$

$$\Delta F_f^\circ_{2400^\circ\text{K}} (\text{ZrC}_{1.0}) = -42.4 \pm 5.5 \text{ kcal gfw}^{-1}$$

$$\Delta F_f^\circ_{2400^\circ\text{K}} (\text{ZrC}_{0.92}) = -40.3 \pm 5.5 \text{ kcal gfw}^{-1}.$$

When the above value for  $\Delta F_f^\circ (\text{NbC}_{0.75})$  is combined with Rudy's<sup>1</sup> result  $\Delta F_f^\circ (\text{MoC}_{1-x}) - \Delta F_f^\circ (\text{NbC}_{1-x}) = 19 \text{ to } 22 \text{ kcal gfw}^{-1}$ , one obtains

$$\Delta F_f^\circ (\text{MoC}_{1-x}) = -6.0 \pm 3.5 \text{ kcal gfw}^{-1}.$$

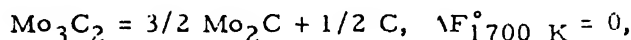
The above value for  $\Delta F_f^\circ (\text{ZrC}_{0.92})$  has been combined with the result of Wallace and co-workers,<sup>2</sup>

$$\Delta F_f^\circ (\text{MoC}_{0.61}) - \Delta F_f^\circ (\text{ZrC}_{0.92}) = 35.8 \pm 1.0 \text{ kcal gfw}^{-1},$$

to obtain

$$\Delta F_f^\circ (\text{MoC}_{0.61}) = -4.5 \pm 6.5 \text{ kcal gfw}^{-1}.$$

The free energy of formation of  $\text{Mo}_3\text{C}_2$  can also be calculated from  $\Delta F_f^\circ (\text{Mo}_2\text{C})$  and the result of Wallace et al<sup>2</sup> that  $\text{Mo}_3\text{C}_2$  disproportionates to  $\text{Mo}_2\text{C}$  and C at  $1450 \pm 100^\circ\text{C}$ . If the disproportionation temperature is taken as  $1700^\circ\text{K}$ , then for the reaction



and hence

$$1/3 \Delta F_f^\circ (\text{Mo}_3\text{C}_2) = 1/2 \Delta F_f^\circ (\text{Mo}_2\text{C})$$

at  $1700^\circ\text{K}$ . The free energy of formation of  $\text{Mo}_2\text{C}$  given in the present report is  $-14.76 \text{ kcal gfw}^{-1}$  at  $1700^\circ\text{K}$ . From this, one obtains the result

$$1/3 \Delta F_f^\circ (\text{Mo}_3\text{C}_2) = -7.38 \text{ kcal gfw}^{-1}.$$

Since this value lies well within the limits of the recalculated values from Wallace's and Rudy's data, it is used in the preparation of the tables for  $\text{Mo}_3\text{C}_2$ .

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### 14. 3 Molybdenum Nitrides

The nitrides of molybdenum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 14. 4 Molybdenum Oxides

During the present project, no new investigations of molybdenum oxides were made. The earlier study had included analyses for  $\text{MoO(g)}$ ,  $\text{MoO}_2\text{(s)}$ ,  $\text{MoO}_2\text{(g)}$ ,  $\text{MoO}_3\text{(s,l)}$  and  $\text{MoO}_3\text{(g)}$ . For a discussion of these compounds, see Barriault, R. J. et al, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. I, Vol. 1 (May 1962). Tables for the above compounds are found in volume 2 of this report. However, a continued bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

## 15. Neodymium Compounds

Detailed analyses were not made for these compounds.

### 15.1 Neodymium Borides

The borides of neodymium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 15.2 Neodymium Carbides

The carbides of neodymium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 15.3 Neodymium Nitrides

The nitrides of neodymium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 15.4 Neodymium Oxides

The oxides of neodymium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

## 16. Niobium Compounds

Selected borides, carbides, nitrides, and oxides of niobium were investigated.

### 16.1 Niobium Borides

A detailed analysis is presented for niobium diboride. In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 16.1.1 Niobium Diboride ( $\text{NbB}_{2(s)}$ )

##### a. Phase Data, Crystal Structure, and Melting Point

In their review, Samsonov and Markovskii<sup>1</sup> indicate that five possible niobium boride phases can form, including  $\text{NbB}_2$ ,  $\text{Nb}_3\text{B}_4$ ,  $\text{NbB}$ ,  $\text{Nb}_2\text{B}$ , and  $\text{Nb}_3\text{B}$ . They indicate that  $\text{NbB}_2$  has an hexagonal structure with  $a=3.085 \text{ \AA}$ ,  $c=3.311 \text{ \AA}$ , and  $c/a = 1.071$ . A melting point of  $3000 \pm 50^\circ\text{C}$  ( $3273 \pm 50^\circ\text{K}$ ) is tabulated, presumably from earlier works by Post et al,<sup>2</sup> and Schwarzkopf and Glaser<sup>3</sup>. For  $\text{Nb}_3\text{B}_4$ , they list a rhombic structure,  $a=3.305 \text{ \AA}$ ,  $b=14.08 \text{ \AA}$ , and  $c=3.137 \text{ \AA}$ . For  $\text{NbB}$ , a rhombic structure with  $a=3.298 \text{ \AA}$ ,  $b=8.724 \text{ \AA}$  and  $c=3.166 \text{ \AA}$  is given. Its melting point is listed as  $2000^\circ\text{C}$  ( $2273^\circ\text{K}$ ). No data are given for the lower borides.

Brewer et al<sup>4</sup> (much of whose data was reviewed by Samsonov and Markovskii<sup>1</sup>) had found  $\text{NbB}_2$  to be hexagonal, isomorphous with  $\text{AlB}_2$  (C32 type). It was found to have an appreciable homogeneity range with  $a=3.085 \pm 0.002 \text{ \AA}$ ,  $c=3.311 \pm 0.002 \text{ \AA}$ . For the phase in equilibrium with  $\text{Nb}_3\text{B}_4$ , they found  $a=3.110 \pm 0.002 \text{ \AA}$  and  $c=3.264 \pm 0.002 \text{ \AA}$ . Brewer et al<sup>4</sup> indicate that only  $\text{NbB}$  and  $\text{NbB}_2$  are stable up to the melting point. The phases  $\text{NbB}_m$ ,  $\text{NbB}_n$ , and  $\text{Nb}_3\text{B}_4$  have only limited ranges of stability.

Nowotny et al<sup>5</sup> have also observed a wide homogeneity range for  $\text{NbB}_2$  extending from 65 percent B to 70 percent B. As the boron content increases,  $a$  decreases from  $3.111$  to  $3.093 \text{ \AA}$  while  $c$  increases from  $3.260$  to  $3.305 \text{ \AA}$ .

Nowotny et al<sup>6</sup> give a phase diagram for the Nb-B system. They show  $\text{NbB}$  and  $\text{NbB}_2$  to have congruent melting points of  $2280$  and  $3000^\circ\text{C}$ , respectively.  $\text{Nb}_3\text{B}_2$  and  $\text{Nb}_3\text{B}_4$  had incongruent melting points of  $1860$  and  $2700^\circ\text{C}$ , respectively.

Kaufman et al (p.V-A-3)<sup>7</sup> have reported lattice constant data for four selected source materials of  $\text{NbB}_2$ . Values of  $a=3.111\text{\AA}$ ,  $c=3.261\text{\AA}$ ,  $a=3.107\text{\AA}$ ,  $c=3.282\text{\AA}$ ,  $a=3.1085\text{\AA}$ ,  $c=3.263\text{\AA}$ , and  $a=3.109\text{\AA}$ ,  $c=3.264\text{\AA}$  were found in general agreement with other investigators.

In the present work, thermodynamic tables are generated for the  $\text{NbB}_2$  since more data are available for this composition, and since it is the most refractory phase. A melting point of  $3000^\circ\text{C}$  ( $3273^\circ\text{K}$ ) is accepted in conformance with data tabulated by Samsonov and Markovskii<sup>1</sup> and Nowotny et al.<sup>6</sup>

Conditions for the formation of niobium borides have been discussed by Meerson.<sup>8</sup> A study of the bonding mechanisms has been made by Korshunskii and Genkin.<sup>9</sup> Crystallographic data for  $\text{Nb}_3\text{B}_2$  has been given by Kieffer and Benesovsky.<sup>10</sup>

## b. Thermodynamic Properties

### 1) Entropy and heat content at $298.15^\circ\text{K}$

Westrum<sup>11</sup> has made low temperature ( $7.74$  to  $347^\circ\text{K}$ ) measurements for a sample of  $\text{NbB}_{1.975}$  which weighed  $182.334$  grams. The data yielded  $C_p^\circ, 298.15 = 11.42 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 8.91 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , and  $H_{298.15}^\circ - H_0^\circ = 1620 \text{ cal gfw}^{-1}$ . If these quantities are multiplied by the ratio  $3.0/2.975$  in an attempt to convert to  $\text{NbB}_2$ , one obtains  $C_p^\circ, 298.15 = 11.516 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 8.985 \text{ eu}$ , and  $H_{298.15}^\circ - H_0^\circ = 1633.6 \text{ cal gfw}^{-1}$ . If one assumes that  $0.025$  mole of free boron can be added to give effectively  $\text{NbB}_2$ , one obtains, using data from the present report for free boron,  $C_p^\circ, 298.15 = 11.49 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 8.945 \text{ eu}$ , and  $H_{298.15}^\circ - H_0^\circ = 1627.5 \text{ cal gfw}^{-1}$ . For the present calculations, we use intermediate rounded values  $C_p^\circ, 298.15 = 11.50 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 8.96 \text{ eu}$ , and  $H_{298.15}^\circ - H_0^\circ = 1630 \text{ cal gfw}^{-1}$ .

### 2) High-temperature heat content

Tilleux<sup>12</sup> has measured the heat content of a sample of  $\text{NbB}_2$  supplied by the U. S. Borax and Chemical Corp (Anaheim, Calif.) The experiments were made for the range  $467.90^\circ - 1102.2^\circ\text{K}$  and yielded the enthalpies in table 35.



TABLE 35

ENTHALPIES OF NbB<sub>2</sub> FROM TILLEUX<sup>1,2</sup>

T (°K)	T <sub>ref</sub> (°K)	H <sub>T</sub> <sup>°</sup> - H <sub>ref</sub> <sup>°</sup> (cal gfw <sup>-1</sup> )
467.90	298.84	2296
588.60	298.97	4098
715.10	298.99	6126
843.90	299.10	8560
976.00	299.29	11157
1102.20	299.34	13638

The data were treated to give two forms of the heat-capacity equation:

$$\text{and } C_p^\circ = 11.00 + 0.00938 T - 0.1766 \times 10^{-6} T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

$$C_p^\circ = 9.272 + 0.011116 T \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

The first equation yielded  $C_{p, 298.15}^\circ = 11.81 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  in good agreement with Westrum's low-temperature data.<sup>1,1</sup> The two constant equation yielded  $C_{p, 298.15}^\circ = 12.59 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  which is not in such good agreement.

For the present work, the experimental enthalpies from Tilleux<sup>1,2</sup> as given in table 35 were analyzed by the Shomate method, using  $C_{p, 298.15}^\circ = 11.50 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . The equation obtained was

$$C_p^\circ = 13.004 + 6.9491 \times 10^{-3} T - 3.1784 \times 10^{-5} T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

The enthalpy values calculated from this equation fit the observed experimental enthalpies well, the largest deviation occurring at 715.1°K where the calculated value is 2.1 percent larger than the experimental value. The above equation was used for its range of validity, 298.15 to 1200°K. From 1200°K to the melting point, a linear variation of  $C_p^\circ$  with T was assumed to give a value of  $C_p^\circ = 30.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  at the melting point. The equation obtained is

$$C_p^\circ = 15.983 + 0.0042826 T \text{ cal deg K}^{-1} \text{ gfw}^{-1}, \text{ for } 1200 \text{ to } 3273^\circ \text{K}.$$

The heat of fusion was estimated and rounded off to give 20,000 cal/mole at 3273°K.

The heat capacity of liquid NbB<sub>2</sub> was estimated to be constant and equal to 30.0 cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

### 3) Heat of formation

According to Brewer and Haraldsen,<sup>13</sup> the heat of formation of  $\text{NbB}_2$  is more negative than -36 kcal/gfw. Samsonov<sup>14</sup> quotes a value of  $\Delta H_f^{\circ}{}_{298.15} = -59$  kcal/gfw based on data from Kubaschewskii and Evans.<sup>15</sup> Samsonov<sup>14</sup> used an estimation procedure to establish the heat of formation as -35.5 kcal/gfw.

Preliminary results of vaporization studies for the  $\text{NbB}_2$  system have been reported by Blackburn.<sup>16</sup> He has considered the data too unreliable to perform quantitative calculation.

Kaufman and Clougherty (page VII-C-2)<sup>7</sup> have reported an estimated heat of formation of -59,400 cal/mole based on volume changes in the formation of the boride.

Huber<sup>17</sup> has made a calorimetric determination on a relatively impure sample of  $\text{NbB}_2$  and obtained  $\Delta H_f^{\circ}{}_{298.15} = -41.9$  kcal/mole.

For the present tabulation, the calorimetric value found by Huber<sup>17</sup> is accepted giving  $\Delta H_f^{\circ}{}_{298.15} = -41.9$  kcal/mole. It is very difficult to estimate the uncertainty, but it is believed that this may be in the range 5 to 10 kcal/mole.

### Supplement

The low-temperature data of Westra<sup>11</sup> as reported by Kaufman and Clougherty<sup>18</sup> are given as  $S^{\circ}{}_{298.15} = 8.91$  e. u. for  $\text{NbB}_{1.963}$ . The results do not differ significantly from those given earlier.

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## 16. 2 Niobium Carbides

Detailed analyses are presented for  $\text{NbC}_{(s,l)}$  and  $\text{Nb}_2\text{C}_{(s)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

### 16. 2. 1 Niobium Carbide ( $\text{NbC}_{(s,l)}$ )

#### a. Phase Diagram, Crystal Structure, and Melting Point

The refractory properties of niobium carbide make this material of particular interest in modern technology. Miller<sup>1</sup> has summarized properties of niobium, tantalum, and their compounds. It is to be noted that niobium has a relatively low total cross section for neutron absorption and, hence, compounds of niobium are of importance in the atomic energy field. Douglass and Kunz<sup>2</sup> have indicated that metallic niobium and its alloys have long been considered for aircraft and missile applications. In the nuclear field as higher-temperature reactors were developed, it became necessary to use niobium instead of zirconium even though the latter had a smaller neutron capture cross section.

Storms<sup>3</sup> has summarized much of the available phase data for the Nb-C system. Earlier, Schwarzkopf and Kieffer<sup>4</sup> have shown a tentative phase diagram due to Goldschmidt.<sup>5</sup> This diagram appears to be oversimplified, showing only an NbC phase. Hansen and Anderko<sup>6</sup> discuss both an  $\text{Nb}_2\text{C}$  and NbC phase, but they do not give a complete phase diagram. They indicate that NbC has the cubic NaCl (B1) type structure with lattice parameter  $a = 4.470 \text{ \AA}$ . Melting points of  $3700^\circ$  to  $3800^\circ\text{C}$  by Friederich and Sittig<sup>7</sup> and  $3500^\circ\text{C}$  by Agte and Alterthum<sup>8</sup> have been reported. The first complete phase diagram for the Nb-C system was given by Storms and Krikorian.<sup>9</sup> They show a eutectic at  $2335^\circ\text{C}$  between  $\text{NbC}_{0.08}$  and  $\text{NbC}_{0.39}$ . At  $3090^\circ\text{C}$ ,  $\text{NbC}_{0.52}$  decomposes peritectically to  $\text{NbC}_{0.56}$  + liquid. Nadler and Kempter<sup>10</sup> had found the peritectic to be  $3080^\circ\text{C}$ . Storms and Krikorian further found that the melting point rises as the carbon content increases up to  $\text{NbC}_{0.86}$  at which point a melting temperature maximum of  $3500^\circ\text{C}$  is reached. Then, the melting point falls to  $3250^\circ\text{C}$  with eutectic melting between NbC and carbon. They also showed that congruent vaporization occurs at  $2800^\circ\text{C}$  for a composition of  $\text{NbC}_{0.71}$ . Additional melting data have been given by Nadler and Kempter,<sup>10</sup> who found the maximum to be  $3480^\circ\text{C}$  and the NbC-C eutectic to be  $3220^\circ\text{C}$ . Engelke et al.<sup>11</sup> reported  $3420^\circ\text{C}$  for  $\text{NbC}_{0.92}$ , and Brownlee<sup>12</sup> gave  $3485^\circ\text{C}$  for  $\text{NbC}_{0.95}$ .

Koval'chenko and Samsonov<sup>13</sup> studied the NbC-C section. They find the melting point of NbC to be  $3500^\circ\text{C}$ . However, they report a surprisingly low NbC-C eutectic of only  $2060^\circ\text{C}$ . Kimura and Sasaki<sup>14</sup> have reported the presence of four phases (Nb solid solution;  $\text{Nb}_2\text{C}$ , NbC, and graphite) in the Nb-C system. They reported a eutectic of  $2300^\circ + 20^\circ\text{C}$  in good agreement with Storms and Krikorian's values of  $2335^\circ\text{C}$ .<sup>9</sup> Elliott<sup>15</sup> also observed the hexagonal  $\text{Nb}_2\text{C}$  and cubic NbC phases. He found the eutectic temperature to be somewhat lower at  $2230^\circ\text{C}$ .

For the NbC phase with the fcc structure, Kempter, Storms, and Fries<sup>16</sup> have reported a lattice parameter  $a = 4.4707 \pm 0.0003 \text{ \AA}$ . They have also reported a relation to show the variation of lattice parameter with composition. Brauer and Lesser<sup>17</sup> reported  $a = 4.4690 \text{ \AA}$  for a composition containing excess carbon. They also reported lattice constants for several other compositions

In the calculation of thermodynamic tables for NbC, the melting point accepted is the value of  $3480^\circ\text{C}$  ( $3753^\circ\text{K}$ ) reported by Nadler and Kempter.<sup>10</sup> It is clear that there is some uncertainty in the melting point and melting range for the NbC<sub>1.00</sub> composition, but for the present the value  $3753^\circ\text{K}$  is used.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at $298.15^\circ\text{K}$

It appears that no experimental low-temperature heat capacity data have been published for NbC. Several estimates of  $S_{298.15}^\circ$  have been reported in the literature. Schick *et al*<sup>18</sup> have calculated  $S_{298.15}^\circ = 7.411 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , and  $C_{p,298.15}^\circ = 7.843 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . The method used depended on an empirical calculation to evaluate the Debye temperature of the constituent elements. Kelley and King<sup>19</sup> estimated  $S_{298.15}^\circ$  to be  $9.0 \pm 0.5 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Kaufman<sup>20</sup> estimated  $S_{298.15}^\circ$  to be  $5.70 \times 2 = 11.40 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Krikorian<sup>21</sup> lists an estimate of  $S_{298.15}^\circ = 8.6 \pm 0.5 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . A further estimate of the entropy at  $298.15^\circ\text{K}$  can be made by considering data for the related Ta-TaC system and the V-VC system.

TABLE 36

AUXILIARY DATA TO ESTIMATE ROOM-TEMPERATURE ENTROPY OF NbC

Molecule	$S_{298.15}^\circ$	Source
	cal deg K <sup>-1</sup> gfw <sup>-1</sup>	
Nb	8.58	Clusius <i>et al</i> <sup>22</sup>
Ta	$9.92 \pm 0.04$	Kelley and King <sup>19</sup>
TaC	$10.11 \pm 0.08$	Kelley and King <sup>19</sup>
V	$6.88 \pm 0.05$	Schick <i>et al</i> *
VC	$6.77 \pm 0.03$	Kelley and King <sup>19</sup>

\* Present report, table 243 (volume 2).

From the above data, it is seen that  $S_{298.15}^{\circ}, \text{TaC}$  is 0.19 e.u. greater than that for metallic Ta. Assuming the same relationship for Nb,  $S_{298.15}^{\circ}, \text{NbC} = 8.58 + 0.19 = 8.77$  e.u. would be obtained. From the V-VC data, it would be estimated that the entropy for NbC would be less than that for metallic Nb. That is,  $S_{298.15}^{\circ}, \text{NbC} = 8.58 - 0.11 = 8.47$  e.u. It appears that the best choice would be an intermediate value. The average of the two values is 8.62 e.u. Finally, because of the somewhat closer relationship of niobium and tantalum, the entropy value is rounded off to 8.7 e.u. This final accepted value of  $S_{298.15}^{\circ}, \text{NbC} = 8.7$  e.u. is probably subject to an uncertainty of  $\pm 0.5$  e.u.

No experimental determination of the heat content at 298.15°K ( $H_{298.15}^{\circ} - H_0^{\circ}$ ) has been available. The only estimate is by Schick et al<sup>18</sup> which is that of  $H_{298.15}^{\circ} - H_0^{\circ} = 1.258$  kcal gfw<sup>-1</sup>. This value is estimated to be subject to an uncertainty of  $\pm 0.150$  kcal gfw<sup>-1</sup>.

## 2) High-temperature heat content

Until recently, there had been no reported high-temperature heat-capacity data for NbC. Thus, Kelley<sup>23</sup> shows no data for this material. Gel'd and Kusenko<sup>24</sup> reported heat-capacity data for niobium oxide, niobium metal,  $\text{NbC}_{0.50}$ ,  $\text{NbC}_{0.749}$ ,  $\text{NbC}_{0.867}$ , and NbC. Additional references to the above work have been made by the same authors.<sup>25, 26</sup> For NbC, the heat-capacity equation found for the range of 298.15° to 1840°K is given by Gel'd and Kusenko<sup>24</sup> as

$$C_p^{\circ} = 10.79 + 1.726 \times 10^{-3} T - 2.15 \times 10^{-5} T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Their equation gives  $C_{p,298.15}^{\circ} = 8.886$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>. Neel et al<sup>27</sup> have made drop measurements for NbC from 495° to 4740°F (530.3° to 2888.7°K) to a reference temperature of 32°F (273.15°K). Their originally derived heat-capacity equation

$$C_p^{\circ} = 100.5 \times 10^{-3} + 12.994 \times 10^{-6} t - 0.3462 \times 10^{-9} t^2 \text{ Btu lb}^{-1} \text{ }^{\circ}\text{F}^{-1},$$

where  $t = ^{\circ}\text{F}$ ,

has subsequently been modified by Pears et al<sup>28</sup> to give

$$C_p^{\circ} = 0.107 + 8.92 \times 10^{-6} t - 5429.6 t^{-2} \text{ Btu lb}^{-1} \text{ }^{\circ}\text{F}^{-1},$$

where  $t = ^{\circ}\text{F}$

The actual enthalpy values found by Neel et al<sup>27</sup> have been recomputed to cgs units and are given in table 37. Assuming that the average  $C_p^{\circ} = 8.5$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> from 273.15° to 298.15°K, a

relatively small correction of 212 cal/mole is made to give  $H_T^\circ - H_{298.15}^\circ$  values.

TABLE 37

CONVERTED HEAT-CONTENT DATA OF NEEL et al<sup>27</sup>

Temperature	$H_T^\circ - H_{273.15}^\circ$	$H_T^\circ - H_{298.15}^\circ$	$H_T^\circ - H_{298.15}^\circ$ (Kusenko and Gel'd)
°K	cal/mole	cal/mole	cal/mole
530.37	1725.3	1513.3	2356
546.48	1917.7	1705.7	2533
814.81	5514.1	5302.1	5614
820.92	4826.3	4614.3	5686
1077.03	8393.6	8181.6	8807
1368.70	12182.4	11970.4	12527
1632.59	14921.9	14709.9	16033
1918.70	19585.1	19373.1	19977
2199.81	24073.3	23861.3	23995
2560.92	28678.1	28466.1	29361
2566.48	29377.6	29165.6	29446
2888.70	33749.3	33537.3	34430

Additional heat-capacity measurements for NbC have been made by a pulse-heating technique reported by Barriault et al.<sup>29</sup> These data covered a range of 1763° to 2529°K. Evidence for a possible transition at 2437°K was noted. These data showed a relatively small change of  $C_p^\circ$  with temperature and gave values considerably larger than Debye lattice theory would predict.



For the present analysis, the data given by Gel'd and Kusenko<sup>24</sup> are adopted. For liquid NbC, the heat capacity is assumed constant and equal to the value of the solid at the melting point; i.e.,  $C_p^0 = 17.252 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Since no heat-of-fusion data are available, this value has been estimated by assuming the entropy of fusion to be  $3 \text{ cal deg K}^{-1} \text{ g atom}^{-1}$  or  $6 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Thus, the heat of fusion is derived to be  $22,518 \text{ cal gfw}^{-1}$ . This is rounded off to give  $22000 \pm 5000 \text{ cal gfw}^{-1}$ . Here, the uncertainty has been estimated.

### 3) Heat of formation

In recent years, there have been several calorimetric determinations of the heats of formation of niobium oxides and carbides. Mah and Boyle<sup>30</sup> found  $\Delta H_{f298.15, \text{NbC}}^{0.9445} = -31.75 \pm 0.8 \text{ kcal/mole}$ . They extrapolated to the stoichiometric composition to give  $\Delta H_{f298.15, \text{NbC}}^0 = -33.6 \pm 0.8 \text{ kcal/mole}$ . Huber et al.<sup>31</sup> studied a range of compositions from NbC<sub>0.489</sub> to NbC<sub>0.984</sub>. They extrapolated their data to NbC to give  $\Delta H_{f298.15, \text{NbC}}^0 = -33.6 \pm 0.6 \text{ kcal/mole}$ . In their analysis, they used  $\Delta H_{f298.15, \text{Nb}_2\text{O}_5}^0 = -455.2 \pm 0.6 \text{ kcal/mole}$ . Kornilov, Leonidov, and Skuratov<sup>32</sup> used a heat of formation of Nb<sub>2</sub>O<sub>5</sub> equal to  $-453.5 \pm 0.4 \text{ kcal/mole}$  to obtain  $\Delta H_{f298.15, \text{NbC}}^{0.913} = -31.0 \pm 0.6 \text{ kcal/mole}$ . Then, assuming the heat of solution of niobium in the carbide phase is zero, they obtained  $\Delta H_{f298.15, \text{NbC}}^0 = -34.0 \pm 0.6 \text{ kcal/mole}$ . Kusenko and Gel'd<sup>33</sup> had earlier obtained heats of combustion data about 1 kcal more negative than the data of Huber et al.<sup>31</sup> Thus, Kusenko and Gel'd<sup>26</sup> summarized these results to give  $\Delta H_{f298.15, \text{NbC}}^0 = -34.8 \text{ kcal/mole}$  and  $\Delta H_{f298.16, \text{Nb}_2\text{C}}^0 = -45.4 \text{ kcal/mole}$ .

For the present analysis, the data of Huber et al.<sup>31</sup> are accepted, giving  $\Delta H_{f298.15, \text{NbC}}^0 = -33.6 \pm 0.8 \text{ kcal/mole}$ . This value is seen to be in good agreement with other determinations.

Several other related references dealing with equilibrium properties of systems, including NbC, might be considered as secondary sources of information regarding thermochemical data for NbC. Many of them are concerned with the Nb-C-O systems. A few typical references include the works of Sazhin et al.,<sup>34</sup> Shveikin,<sup>35</sup> Shveikin, Gel'd, and Alyamovskii,<sup>36</sup> and Gel'd and Liubimov.<sup>37</sup>

### 4. Vaporization data

It is generally considered that NbC vaporizes to yield atomic species. Bolgar, Verkhoglyadova, and Samsonov<sup>38</sup> studied the vaporization and concluded that molecular species are formed. However, Storms<sup>3</sup>

has pointed out that their conclusion is not valid. Storms and Krikorian<sup>9</sup> have shown that NbC<sub>0.71</sub> vaporizes congruently at a temperature of 2800°C. A fairly comprehensive study of vaporization properties has recently been made by Fries.<sup>39</sup> He found that NbC<sub>0.75</sub> vaporizes congruently at 2940°K.

### Supplement

Levinson<sup>40</sup> reported heat-content measurements for NbC<sub>0.97</sub> for the range 1289° to 2778°K. These data could not be incorporated into the present work because of time limitations.

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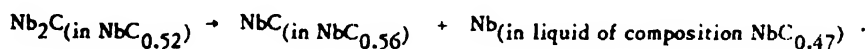
## 16.2.2 Diniobium Carbide ( $\text{Nb}_2\text{C}_{(s)}$ )

### a. Phase Diagram, Crystal Structure, and Decomposition Point (Peritectic)

In the discussion of the NbC phase, the relevant references for the phase data of the entire Nb-C system will be discussed in section IVB15.2.1. For completeness, that discussion should be consulted. From the works of Storms,<sup>1</sup> and Storms and Krikorian,<sup>2</sup> and earlier works, it has been found that the  $\text{Nb}_2\text{C}$  phase has an hcp structure. This phase shows a narrow range of homogeneity at low temperatures which broadens rapidly above 2000°C. Finally at 3090°C, peritectic decomposition of  $\text{NbC}_{0.52}$  into  $\text{NbC}_{0.56}$  plus liquid occurs.

Lattice constants reported by Storms and Krikorian<sup>2</sup> for  $\text{NbC}_{0.50}$  are  $a = 3.128 \pm 0.001 \text{ \AA}$  and  $c = 4.972 \pm 0.001 \text{ \AA}$ .

According to Storms and Krikorian,<sup>2</sup> the peritectic decomposition of  $\text{Nb}_2\text{C}$  at 3363°K ( $3090 \pm 50^\circ\text{C}$ ) can be represented as:



In the present work, this peritectic temperature of 3363°K is accepted as it is in good agreement with the value of 3353°K found by Nadler and Kempter.<sup>3</sup> Elliott<sup>4</sup> has also noted the same type of peritectic behavior.

In preparing thermochemical tables, the peritectic temperature reported by Storms and Krikorian<sup>2</sup> is accepted in lieu of a melting point. The tables are calculated to this temperature. Immediately above this temperature, a system of overall composition  $\text{Nb}_2\text{C}$  will be a two-phase system containing a liquid phase and an  $\text{NbC}_{1-x}$  phase.

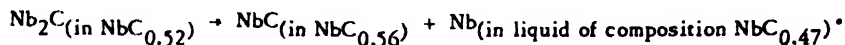
### b. Thermodynamic Properties

#### 1) Low-temperature heat capacity and entropy at 298.15°K

There are no reported experimental data for the low-temperature heat capacity and entropy at 298.15°K for  $\text{Nb}_2\text{C}$ . Accordingly, it is necessary to attempt to estimate these data. Schick *et al*<sup>5</sup> used empirically estimated Debye temperatures to calculate that  $S_{298.15}^\circ, \text{Nb}_2\text{C} = 15.177 \text{ e.u.}$ ,  $C_{p,298.15}^\circ = 14.085 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , and  $H_{298}^\circ - H_0^\circ = 2.472 \text{ kcal gfw}^{-1}$ . Krikorian<sup>6</sup> has estimated  $S_{298.15}^\circ, \text{Nb}_2\text{C} = 18.4 \pm 1.0 \text{ e.u.}$  Gel'd and Kusenko<sup>7</sup> have estimated  $S_{298.15}^\circ, \text{Nb}_2\text{C} = 17.48 \text{ e.u.}$  by assuming that  $\Delta S^\circ = 0$  for the reaction:



To relate the entropy value for  $\text{Nb}_2\text{C}$  as closely as possible to observed experimental data, one can refer to the equilibrium phase diagram for the Nb-C system given by Storms and Krikorian.<sup>2</sup> As mentioned earlier, they have found that peritectic decomposition occurs at 3363°K:



In the above, it is noted that  $\text{Nb}_2\text{C}$  in the  $\text{NbC}_{0.52}$  has a composition close to stoichiometric. However, NbC in  $\text{NbC}_{0.56}$  can be written as  $\text{Nb}_{0.44}(\text{NbC})_{0.56}$ . In this case, the mole fraction of the NbC in the  $\text{NbC}_{0.56}$  is given as  $x_{\text{NbC}} = 0.56$ . Also, the mole fraction of Nb in the liquid  $\text{NbC}_{0.47}$  is given as  $x_{\text{Nb}} = 1/1.47 = 0.68$ . If it is assumed that Raoult's law applies, then the activities can be considered equal to the mole fractions. Thus,

$a_{\text{Nb}_2\text{C}}$	1
$a_{\text{NbC}}$	0.56
$a_{\text{Nb}}$	0.68

From these data, the free-energy change for the peritectic decomposition at 3363°K becomes

$$\Delta F_{(\text{reaction}, 3363^\circ\text{K})}^\circ = -RT \ln \left( \frac{a_{\text{Nb}} a_{\text{NbC}}}{a_{\text{Nb}_2\text{C}}} \right) = 6.465 \text{ kcal/mole.}$$

From the tabulated data for NbC,  $\Delta F_{f3300^\circ\text{K}}^\circ \text{NbC} = -31.079$  and  $\Delta F_{f3400^\circ\text{K}}^\circ \text{NbC} = -30.897 \text{ kcal/mole}$ . Interpolating,  $\Delta F_{f3363^\circ\text{K}}^\circ = -30.965 \text{ kcal/mole}$ .

Combining the  $\Delta F^\circ$  data for the peritectic reaction and the free energy of formation of NbC, the free energy of formation of  $\text{Nb}_2\text{C}$  is obtained as

$$\Delta F_{f\text{Nb}_2\text{C}, 3363^\circ\text{K}}^\circ = -30.965 - 6.465 = -37.430 \text{ kcal/mole.}$$

If this value of the free energy of formation of  $\text{Nb}_2\text{C}$  at 3363°K is accepted, it can be combined with the calorimetric heat of formation of  $\text{Nb}_2\text{C}$  ( $\Delta H_{f298.15}^\circ = -46.6 \text{ kcal/mole}$ ) from Huber et al<sup>8</sup> and free-energy functions for Nb and C to calculate the free-energy function of  $\text{Nb}_2\text{C}$ . Then using the known high-temperature heat-capacity data for  $\text{Nb}_2\text{C}$  from Gel'd and Kusenko,<sup>7</sup> the entropy at 298.15°K can be evaluated. The standard free energy of formation of  $\text{Nb}_2\text{C}$  is given as

$$\begin{aligned}
\Delta F_f^\circ &= \Delta H_{f298.15}^\circ - T (f_{\text{Nb}_2\text{C}} - 2 f_{\text{Nb}} - f_{\text{C}}) \\
&- \left( \frac{F_T^\circ - H_{298.15}^\circ}{T} \right)_{\text{Nb}_2\text{C}} = (f_{\text{Nb}_2\text{C}}) - \frac{\Delta H_{f298.15}^\circ}{T} - \frac{\Delta F_f^\circ}{T} + 2 f_{\text{Nb}} + f_{\text{C}} \\
&= \frac{-46,600}{3363} - \frac{(-37430)}{3363} + 2(19.318) + 7.881 \\
&= -13.8566 + 11.1299 + 38.636 + 7.881
\end{aligned}$$

$$(f_{\text{Nb}_2\text{C}}) = 43.790 \text{ e.u.}$$

From the above value of  $(f_{\text{Nb}_2\text{C}})$ ,  $3363^\circ\text{K} = 43.790 \text{ e.u.}$ , it is found that use of the Gel'd and Kusenko <sup>7</sup> heat-capacity equation  $C_{p,\text{Nb}_2\text{C}}^\circ = 15.88 + 3.0 \times 10^{-3} T - 2.050 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  leads to  $S_{3363}^\circ - S_{298}^\circ = 47.672 \text{ e.u.}$  and  $H_{3363}^\circ - H_{298}^\circ = 65.501 \text{ kcal/gfw.}$

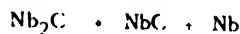
Therefore,

$$\begin{aligned}
(f_{\text{Nb}_2\text{C}}) &= - \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right) = S_{298}^\circ + (S_T^\circ - S_{298}^\circ) - \left( \frac{H_T^\circ - H_{298}^\circ}{T} \right), \text{ and} \\
S_{298}^\circ &= (f_{\text{Nb}_2\text{C}}) - (S_T^\circ - S_{298}^\circ) + \left( \frac{H_T^\circ - H_{298}^\circ}{T} \right) \\
&= 43.790 - 47.672 + \frac{65501}{3363} \\
&= 43.790 - 47.672 + 19.4769
\end{aligned}$$

$$S_{298}^\circ = 15.595 \text{ e.u.}$$

In the above calculations, it can be noted that if the experimental  $S_{298.15}^\circ$  value for elemental niobium is used ( $S_{298.15}^\circ = 8.58 \text{ e.u.}$  rather than the value  $9.0 \text{ e.u.}$  actually used in the present tables (table 173); then  $S_{298.15,\text{Nb}_2\text{C}}^\circ$  is reduced, by  $9.0 - 8.58 = 0.42 \text{ e.u.}$ , from  $15.595$  to  $15.175 \text{ e.u.}$  It is to be noted that the contribution of a single mole of Nb is effective here since the quantity  $\Delta F_{f\text{Nb}_2\text{C}}^\circ = -37430 \text{ cal/mole}$  has been calculated by using  $\Delta F_{f\text{NbC}}^\circ = -30965 \text{ cal/mole}$  and using the free-energy function for a single mole of niobium. Hence, this expression cancels one-half of the contributions from the expression " $2f_{\text{Nb}}$ " earlier.

If the basic peritectic reaction were studied, the important terms in the summation would be more evident:



$$\Delta F^\circ_{\text{reaction}, 3363^\circ\text{K}} = \Delta H^\circ_{298.15} - T (\text{fef}_{\text{NbC}} + \text{fef}_{\text{Nb}} - \text{fef}_{\text{Nb}_2\text{C}})$$

$$\begin{aligned} \text{Here } \Delta H^\circ_{298.15} &= \Delta H^\circ_{f, \text{NbC}, 298.15} - \Delta H^\circ_{f, \text{Nb}_2\text{C}, 298.15} \\ &= -33.6 - (-46.6) = +13.0 \text{ kcal/mole.} \end{aligned}$$

$$\begin{aligned} \text{fef}_{\text{Nb}_2\text{C}} &= \frac{\Delta F^\circ_{\text{reaction}}}{3363} - \frac{\Delta H^\circ_{298.15}}{3363} + \text{fef}_{\text{NbC}} + \text{fef}_{\text{Nb}} \\ &= \frac{6465}{3363} - \frac{13,000}{3363} + 26.416 + 19.318 \\ &= 1.9224 - 3.8655 + 26.416 + 19.318 \end{aligned}$$

$$\text{fef}_{\text{Nb}_2\text{C}} = 43.790 \text{ e.u.}$$

This value for the free-energy function of  $\text{Nb}_2\text{C}$  is identical to that used earlier. However, now the contributions from the various terms are more obvious. Thus, if  $\text{fef}_{\text{Nb}}$  is reduced from 19.318 to 18.898 e. u., then  $\text{fef}_{\text{Nb}_2\text{C}}$  is reduced from 43.790 to 43.370 e. u. and, hence,  $S^\circ_{298.15, \text{Nb}_2\text{C}}$  becomes 15.175 e. u. as discussed earlier.

If  $\Delta F^\circ_{\text{reaction}}$  has an uncertainty of about 3000 cal/mole, thus, an uncertainty of 1.0 e. u. is contributed.

Other possible uncertainties are listed below:

	Uncertainty in $\text{fef}_{\text{Nb}_2\text{C}}$
	e. u.
Uncertainty in $\Delta F^\circ_{\text{reaction}, 298.15}$	$\pm 1.0$
Uncertainty in $\Delta H^\circ_{\text{reaction}, 298.15}$	$\pm 0.3$
Uncertainty in $\text{fef}_{\text{NbC}}$	$\pm 1.5$
Uncertainty in $\text{fef}_{\text{Nb}}$	$\pm 1.5$
Total Uncertainty in $\text{fef}_{\text{Nb}_2\text{C}}$	$\pm 4.3$

Thus, one can see that the total uncertainty in  $\text{fef}_{\text{Nb}_2\text{C}}$  may be as much as  $\pm 4.3$  e. u. from the high-temperature equilibrium data and, therefore, the derived value of  $S^\circ_{298.15}$  will also be subject to a comparable uncertainty.

As another approach to estimation of the entropy of  $\text{Nb}_2\text{C}$ , one can utilize known entropies of formation of carbides. In table



38, some available entropy-of-formation data are summarized. It is seen that the entropy of formation of NbC from elemental niobium and carbon has been estimated to be -1.24 e. u. For the related molecules TaC and VC, the corresponding values are -1.17 and -1.61 e. u., respectively. There is little additional information to estimate the entropy of the reaction:



TABLE 38

SOME ENTROPIES OF FORMATION OF CARBIDES

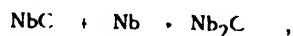
[All Data from Kelley and King<sup>9</sup> except When Noted]  
(All Quantities in e. u. --298.15°K)

Compound (Me <sub>x</sub> C)	S <sub>Me<sub>x</sub>C</sub> <sup>o</sup>	S <sub>Me</sub> <sup>o</sup>	x·S <sub>Me</sub> <sup>o</sup>	S <sub>C</sub> <sup>o</sup>	ΔS
B <sub>4</sub> C	6.47	1.403	5.612	1.36	-0.502
Cr <sub>1.4</sub> C	10.21	5.68	8.52	1.36	-0.33
Mn <sub>3</sub> C	23.6	7.64	22.92	1.36	-0.68
SiC <sub>(hex)</sub>	3.94	4.51	4.51	1.36	-1.93
TaC	10.11	9.92	9.92	1.36	-1.17
TiC	5.79	7.30	7.30	1.36	-2.87
VC	6.77	7.02	7.02	1.36	-1.61
ZrC	7.964*	9.32	9.32	1.36	-2.716
NbC	8.7*	8.58**	8.58	1.36	-1.24

\* Data used in present report.

\*\* Data from Clusius, Franzosini, and Piesbergen.<sup>10</sup>

However for the present case, it would appear that  $\Delta S^\circ$  would be between -1.24 and 0 e. u. If  $\Delta S^\circ = -1.24$  e. u. then,  $S_{\text{Nb}_2\text{C}, 298.15}^\circ = 16.04$  e. u. If  $\Delta S^\circ = 0$  then,  $S_{\text{Nb}_2\text{C}, 298.15}^\circ = 17.28$  e. u. Reference to the phase diagram of Storms and Krikorian<sup>2</sup> shows that  $\text{NbC}_{0.86}$  has a maximum melting point of 3500°C, whereas decreased stability is shown by compositions on either side; i. e.,  $\text{Nb}_2\text{C}$  and  $\text{NbC}$  both have lower melting points. Thus, it seems entirely possible that the entropy of the reaction:



could be -1.24 e. u. and, hence, the entropy of  $\text{Nb}_2\text{C}$  would be about 16.0 e. u.

From the various considerations thus far discussed, and from the various reported estimates, it appears that an entropy of  $\text{Nb}_2\text{C}$  at 298.15°K; i. e.,  $S_{298.15}^\circ = 16.0$  e. u., would be a reasonable estimate. The uncertainty is estimated to be  $\pm 1.0$  e. u. and, hence, the final recommended value is  $S_{298.15, \text{Nb}_2\text{C}}^\circ = 16.0 \pm 1.0$  e. u. The value of  $H_{298}^\circ - H_0^\circ = 2.472$  kcal gfw<sup>-1</sup> estimated by Schick et al<sup>5</sup> is the only estimate available and is used.

## 2) High-temperature heat-capacity data

It has been noted earlier that Gel'd and Kusenko<sup>7</sup> have made heat-capacity measurements for  $\text{Nb}_2\text{C}$  for the range of 298.15° to 1890°K. They have reported an equation of the form:

$$C_{P, \text{NbC}_{0.5}}^\circ = 7.94 + 1.50 \times 10^{-3}T - 1.025 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1},$$

or

$$C_{P, \text{Nb}_2\text{C}}^\circ = 15.88 + 3.0 \times 10^{-3}T - 2.050 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

This equation has been accepted for the present work and extrapolated to the peritectic decomposition temperature.

## 3) Heat of formation

Oxygen bomb calorimetry has been used by Huber et al<sup>8</sup> to study a range of compositions. They have obtained the heat of formation of  $\text{Nb}_2\text{C}$  as  $\Delta H_{1298.15}^\circ = -46.6$  kcal gfw<sup>-1</sup>. Kusenko and Gel'd<sup>11, 12</sup> also have studied a range of compositions including  $\text{NbC}$ ,  $\text{NbC}_{0.99}$ ,  $\text{NbC}_{0.936}$ ,  $\text{NbC}_{0.877}$ ,  $\text{NbC}_{0.749}$ , and  $\text{NbC}_{0.147}$ . Their data have been found to be in general agreement with the data of Huber et al.<sup>8</sup> Thus, Kusenko and Gel'd<sup>13</sup> have given  $\Delta H_{1298.15, \text{Nb}_2\text{C}}^\circ = -45.4$  kcal gfw<sup>-1</sup>.

which is in good agreement with the Huber et al<sup>8</sup> results. For the present case, the data of Huber et al are used. The choice of their data is also preferred in maintaining consistency with the earlier choice of their data for the NbC composition.

#### 4) Vaporization Data

Fries<sup>14</sup> has made a fairly comprehensive study of the vaporization properties of the Nb-C system. From his observation that NbC<sub>0.75</sub> vaporizes congruently at 2940°K, it would be expected that NbC<sub>0.50</sub> (Nb<sub>2</sub>C) compositions would lose niobium preferentially. Additional vaporization data for the Nb-C system have been reported in the section devoted to NbC.

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## 16.3 Niobium Nitrides

### Phase Diagram and General Information

Hansen and Anderko<sup>1</sup> do not give a phase diagram for the Nb-N system. However, they do summarize available data to 1958. They indicate that the NbN phase can exist in three modifications: NbN I is hexagonal with  $a = 2.956\text{\AA}$ ,  $c = 11.27\text{\AA}$ ,  $c/a = 3.815$ ; NbN II is also hexagonal with  $a = 2.94\text{\AA}$ ,  $c = 5.46\text{\AA}$ ,  $c/a = 1.86$ , although NbN II apparently has only a limited degree of stability; and NbN III has the NaCl-type structure with  $a = 4.389\text{\AA}$ . A phase containing 42.9 to 44.1 atom-percent N has a tetragonally distorted NaCl structure with  $a = 4.386\text{\AA}$ ,  $c = 4.312\text{\AA}$ , and  $c/a = 0.983$  at 42.9 atom percent N.

Nb<sub>2</sub>N has an hcp structure of Nb atoms with N atoms located in interstitial positions. A more recent review of the Nb-N system has been made by Storm.<sup>2</sup> He considers NbN to exist in three stable forms.

- $\gamma$ -NbN      (tetragonal) (appears related to  $\delta$  phase but data are uncertain),
- $\delta$ -NbN      (fcc)              (stable above 1370°C), and
- $\epsilon$ -NbN      (hexagonal) (stable below 1370°C).

The hexagonal Nb<sub>2</sub>N phase exists between NbN<sub>0.40</sub> and NbN<sub>0.50</sub> according to Brauer and Esselborn.<sup>3</sup> Storms<sup>2</sup> does not show a phase diagram for the Nb-N system. However, Elliott and Komjathy<sup>4</sup> have given a "probable form of the Nb-N phase equilibrium at one atmosphere nitrogen." This diagram shows the hexagonal NbN to be stable to 1300°C. Above 1300°C, the fcc form of NbN becomes the stable phase which persists to  $\approx 2200^\circ\text{C}$  (2473°K). The other intermediate phase shown in this diagram is the Nb<sub>2</sub>N phase which is considered stable to  $\approx 2400^\circ\text{C}$  (2673°K).

The available data thus indicate that there are many uncertainties in the Nb-N system regarding structures, transitions, and ranges of homogeneity. Most of the available work does indicate that only two compositions lead to compound formation; namely, NbN and Nb<sub>2</sub>N. However, Brauer and Esselborn<sup>3</sup> also favor the possibility of the  $\gamma$ -phase Nb<sub>4</sub>N<sub>3</sub>. Further phase data have been given by English<sup>5</sup> to 60 atom-percent nitrogen.

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### 16.3.1 Niobium Nitride (NbN<sub>(s,l)</sub>)

#### a. Crystal Structure, Transition Point, and Melting Point

As indicated in the general discussion, NbN exists in several modifications. Incomplete agreement has resulted from the works of various investigators and reviewers.<sup>1-4</sup> In the present work, it is considered that  $\epsilon$ -NbN, with an hexagonal structure ( $a = 2.9591 \pm 0.0002\text{\AA}$ ,  $c = 11.2714 \pm 0.0006\text{\AA}$ ) from the work of Brauer and Esselborn<sup>3</sup> and in accord with Storms<sup>2</sup> and Elliott and Komjathy,<sup>4</sup> is the stable low-temperature form. Storms indicates that  $\gamma$ -NbN with an fcc structure is stable above 1370°C. This is in general accord with the viewpoint of Elliott and Komjathy,<sup>4</sup> who indicate that as the temperature is raised a transition occurs from the hexagonal to fcc form of NbN at 1300°C. For the present work, the transition temperature is considered to be 1370°C (1643°K).

There appears to be no precise information on the melting temperature of NbN. The work of Elliott and Komjathy<sup>4</sup> indicates that melting may occur near 2200°C (2473°K). Friederich and Sittig<sup>5</sup> found melting to occur at 2050°C (2323°K). In the present work, the latter value, which is apparently the only actual experimental measurement, is accepted. It is suggested that a somewhat higher melting point might be expected for this system by analogy with the tantalum-nitrogen system.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

There do not appear to have been any experimental determinations of the low-temperature heat capacity of NbN. Kelley and King<sup>6</sup> estimated  $S_{298.15}^{\circ} = 9.0 \pm 0.5$  e. u. Kaufman<sup>7</sup> estimated  $S_{298.15}^{\circ} = 12.6$  e. u. Schick<sup>8</sup> estimated  $C_{p,298.15}^{\circ} = 10.421$  cal degK<sup>-1</sup> gfw<sup>-1</sup>;  $S_{298.15}^{\circ} = 11.391$  e. u. and  $H_{298.15}^{\circ} - H_0^{\circ} = 1.846$  kcal gfw<sup>-1</sup>. The Latimer<sup>9</sup> procedure has been reviewed by Kubaschewski and Evans.<sup>10</sup> The method does not provide sufficient data immediately to make an estimate. However, if one uses the contributions tabulated for Nb = 12.2 e. u., Zr = 12.1 e. u., and Ti = 9.8 e. u., and if one then calculates the values of N in the compounds TiN and ZrN using  $S_{298.15}^{\circ}$  for these latter two compounds as 7.24 and 9.29 e. u. from Kelley and King,<sup>6</sup> one finds that the N contribution is -2.56 and -2.81 e. u., respectively. If an approximate value of the N contribution of -2.50 e. u. is used, one then calculates  $S_{298.15}^{\circ}, \text{NbN} = 12.2 - 2.5 = 9.7$  e. u. There is a probability that ZrN, and possibly TiN, do not form a perfect lattice at zero deg and hence has residual entropy at 0°K. For example, Smagina and Kutsev<sup>11</sup> have shown the ZrN lattice to contain a large proportion of vacancies. If this disorder persists at 0°K, the absolute entropy of these compounds should be increased somewhat. Hence, the predicted value of entropy for NbN would be larger than 9.7 e. u.

For the present purposes, it appears best to adopt some intermediate value between 9.7 and 11.4 e. u. The final, selected value is taken as 10.5 e. u. Probable uncertainty of this value is considered to be  $\pm 1.0$  e. u.

### 2) High-temperature heat content

Kelley<sup>12</sup> tabulates a heat-capacity equation for NbN based on the work of Sato and Sogabe.<sup>13</sup> This equation is

$$C_p^{\circ} = 8.69 + 5.40 \times 10^{-3} T \text{ cal degK}^{-1} \text{ gfw}^{-1} \text{ for } 273^{\circ}\text{K} \leq T \leq 573^{\circ}\text{K}.$$

This equation gives  $C_{p,298.15}^{\circ} = 10.30$  cal degK<sup>-1</sup> gfw<sup>-1</sup> in excellent agreement with the value estimated by Schick,<sup>8</sup> and  $C_{p,600^{\circ}\text{K}}^{\circ} = 11.93$  cal degK<sup>-1</sup> gfw<sup>-1</sup>.

For the interval 600° to 1643°K, an estimated, linear heat-capacity relation has been used. It was assumed that at 1643°K the heat capacity has attained a value of 14.0 cal degK<sup>-1</sup> gfw<sup>-1</sup>. The equation derived is

$$C_p^\circ = 10.7391 + 0.0019847 T \text{ cal deg K}^{-1} \text{ gfw}^{-1} \text{ for } 600^\circ\text{K} \leq T \leq 1643^\circ\text{K}.$$

For the transition from the low-temperature hexagonal to fcc structures, it is necessary to estimate the heat of transition. There is very little information available to aid in such an estimate. For metals such as titanium, the transition from hcp to fcc involves an entropy of transition of 0.822 e.u. (see Barriault *et al*<sup>14</sup>). According to Hansen and Anderko,<sup>1</sup> TiO exists with the fcc structure which may transform at higher temperatures into a phase whose structure is not clearly identified. According to Kelley,<sup>12</sup> the transition occurs at 1264°K with a heat of transition of 820 cal/gfw. In view of the large uncertainties, it is estimated that the transition of NbN requires 820 kcal gfw<sup>-1</sup> at 1643°K. It is clear that this is subject to an uncertainty of approximately  $\pm 1.0$  kcal gfw<sup>-1</sup>.

Above 1643°K, it is assumed that the heat capacity is constant with a value of  $C_p^\circ = 15.0$  cal degK<sup>-1</sup> gfw<sup>-1</sup>.

At the adopted melting point of 2325°K, it is assumed that the entropy of fusion is 2.5 cal degK<sup>-1</sup> g atom<sup>-1</sup>, or 5.0 cal degK<sup>-1</sup> gfw<sup>-1</sup>. This leads to a heat of fusion of 11,615 cal gfw<sup>-1</sup> which is rounded off to 11,000 cal gfw<sup>-1</sup>. The latter value is accepted herein.

For molten TiN, the heat capacity is estimated to be 15.0 cal degK<sup>-1</sup> gfw<sup>-1</sup>. This value is extrapolated to the limit of the table; i. e., 6000°K, realizing, of course, that the liquid phase may not be stable under ordinary pressures for very high temperatures.

### 3) Heat of formation

Mah and Gellert<sup>15</sup> used combustion calorimetry to find that  $\Delta H_{f298.15}^\circ = -56.8 \pm 0.4$  kcal gfw<sup>-1</sup> for NbN. The calculation had used a heat-of-formation value for Nb<sub>2</sub>O<sub>5</sub> of -455.2 kcal gfw<sup>-1</sup>. Using the value -454.000 kcal gfw<sup>-1</sup> accepted in the present work, it is found that  $\Delta H_{f298.15}^\circ \text{NbN} = -56.5$  kcal gfw<sup>-1</sup>. Ehl, Sime, and Margrave<sup>16</sup> listed two other older sources, Brewer *et al*<sup>17</sup> and Neumann *et al*,<sup>18</sup> as having found  $\Delta H_{f298.15}^\circ = -59.0$  kcal deg<sup>-1</sup>. For the present work, the recalculated value of Mah and Gellert;<sup>15</sup> i. e.,  $\Delta H_{f298.15}^\circ = -56.5 \pm 0.4$  kcal gfw<sup>-1</sup> is used.



#### 4) Vaporization data

There do not appear to have been any comprehensive vaporization studies for the NbN phase. Brauer and Esselborn<sup>3</sup> noted that at 1400°C (1673°K) the N<sub>2</sub> pressure of NbN<sub>0.98</sub> was over 760 mm Hg, while NbN<sub>0.88</sub> at the lower phase boundary exerted an N<sub>2</sub> pressure of about 200 mm Hg. Studies by Pemsler<sup>19,20</sup> and Cost and Wert<sup>21</sup> pertained to the Nb-N system in the region Nb-Nb<sub>2</sub>N, and hence are not applicable to the NbN phase. Samsonov and Verkhoglyadova<sup>22</sup> made measurements with the Langmuir method. They found an expression of the form  $\log P = 5.1 - \frac{20,000}{T}$ . \* This would indicate an approximate value of  $\Delta H_{\text{reaction}} = 91.5 \text{ kcal/mole N}_2$ . By comparison, the heats of reaction calculated from the present tables assuming  $2\text{NbN} \rightarrow 2\text{Nb} + \text{N}_2$  are about +103 kcal/mole N<sub>2</sub> at 2000°K, and for the reaction  $4\text{NbN} \rightarrow 2\text{Nb}_2\text{N} + \text{N}_2$ , the heat of reaction is 100 kcal/mole N<sub>2</sub>. It would appear that the Samsonov and Verkhoglyadova<sup>22</sup> data are qualitatively correct, but no detailed analysis of their work has been made.

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\*Units of P not given; however, the heat of reaction can still be calculated from the second half of the right-hand side of the equation.

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### 6. 3. 2 Diniobium Nitride (Nb<sub>2</sub>N(s))

#### a. Crystal Structure and Melting Point

In the general discussion, it was indicated that Nb<sub>2</sub>N has an hcp structure. Brauer and Esselborn<sup>1</sup> indicated that this phase exists in the range NbN<sub>0.40</sub> to NbN<sub>0.50</sub>. Exact details of the variation of the homogeneity range with temperature are not known. Elliott and Komjathy<sup>2</sup> indicate that this phase melts near 2400°C (2673°K).

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at 298.15°K

There appear to be no experimental determinations of the low-temperature heat-capacity data for Nb<sub>2</sub>N. Schick<sup>3</sup> has estimated that  $C_p^\circ, 298.15 = 16.13 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ ,  $H_{298.15}^\circ - H_0^\circ = 2.938 \text{ kcal gfw}^{-1}$ , and  $S_{298.15}^\circ = 18.339 \text{ e. u.}$

From the value of  $S_{298.15}^\circ = 10.5 \text{ e. u.}$  estimated for NbN, if it is assumed that  $\Delta S^\circ = 0$  for the following reaction,



one calculates that  $S_{298.15}^\circ, \text{Nb}_2\text{N} = S_{\text{NbN}}^\circ + S_{\text{Nb}}^\circ + 0$ ,

$$= 10.5 + 9.0,$$

$$S_{298.15}^\circ, \text{Nb}_2\text{N} = 19.5 \text{ e. u.}$$

The Latimer method, if it is used as already done in the NbN section, and if it is assumed that the N contribution is -2.5 e. u., then  $S_{298.15}^\circ, \text{Nb}_2\text{N} = 2(12.2) - 2.5 = 21.9 \text{ e. u.}$

For the present work, an intermediate entropy value of  $S_{298.15}^\circ = 19.0 \text{ e. u.}$  is accepted. The other estimates made by Schick<sup>3</sup> for  $C_p^\circ, 298.15$  and  $H_{298.15}^\circ - H_0^\circ$  are retained.

##### 2) High-temperature heat content

There appear to have been no experimental determinations of high-temperature heat-capacity data for Nb<sub>2</sub>N. Therefore, some crude estimates have been made. For 298.15°K, the value of  $C_p^\circ = 16.13 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ , already discussed, was accepted. At 1000°K, a value of  $C_p^\circ = 19.0 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  was estimated. This value appeared to be about right based on an estimate of the constant-volume specific heat made by Schick.<sup>3</sup> The latter

value was  $C_v = 17.637 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ . A reasonable correction to constant pressure would thus imply a value of about  $19.0 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ . Similarly, by reference to the specific heat for 2 moles of elemental Nb, one estimates a contribution of  $13.240 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  and if one adds  $6.0 \text{ cal degK}^{-1} \text{ g atom}^{-1}$  because of the nitrogen contribution, one then estimates  $C_p^\circ = 19.240 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  for NbN at  $1000^\circ\text{K}$ . Thus, a value near  $19.0$  seems to be about right. Similar considerations indicated that  $C_{p, 2673^\circ\text{K}}^\circ = 22.5 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ . To fit these estimates, two linear equations were used. The first equation covering the range  $298.15^\circ$  to  $1000^\circ\text{K}$  yielded the following:

$$C_p^\circ = 14.9109 + 0.0040891T \text{ cal degK}^{-1} \text{ gfw}^{-1} \text{ for } 298.15^\circ\text{K} \leq T \leq 1000^\circ\text{K}.$$

For the range  $1000^\circ$  to  $2673^\circ\text{K}$ , the following equation was obtained:

$$C_p^\circ = 16.908 + 2.092 \times 10^{-3}T \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

In view of the many uncertainties, no attempt was made to carry the tables above the melting temperature.

### 3) Heat of formation

A combustion technique was used by Mah<sup>4</sup> to find that  $\Delta H_f^\circ_{298.15} = -61.1 \pm 1.0 \text{ kcal gfw}^{-1}$ . The sample used was treated as a solid solution of 92.33 mole-percent  $\text{Nb}_2\text{N}$  and 7.67 mole-percent  $\text{Nb}_2\text{O}$ . It is thus seen that the sample was relatively impure. In making the calculations, Mah assumed that the heat of formation of  $\text{Nb}_2\text{O}_5$  is  $-455.2 \text{ kcal gfw}^{-1}$ . If the value accepted in the present work of  $-454.6$  is utilized, the heat of formation for  $\text{Nb}_2\text{N}$  is changed to  $-60.5 \text{ kcal gfw}^{-1}$ .

Cost and Wert<sup>5</sup> measured the  $\text{N}_2$  pressure over  $\text{Nb}_2\text{N}$  for the temperature range  $1460^\circ$  to  $2230^\circ\text{C}$  ( $1733^\circ$  to  $2503^\circ\text{K}$ ). From their plots of log pressure versus the reciprocal of temperature, they found  $\Delta H_f^\circ = -67 \text{ kcal/gfw}$ . They apparently did not attempt to reduce these data to  $298.15^\circ\text{K}$ . The average temperature of their experiments is about  $2200^\circ\text{K}$ . Thus, they have found  $\Delta H_f^\circ_{2200} = -67 \text{ kcal gfw}^{-1}$ . To convert to  $298.15^\circ\text{K}$ ,

$$\begin{aligned}
\Delta H_{f298.15}^{\circ} &= \Delta H_{f2200}^{\circ} - (H_{2200}^{\circ} - H_{298}^{\circ})_{\text{Nb}_2\text{N}} + 2(H_{2200}^{\circ} - H_{298}^{\circ})_{\text{Nb}} \\
&\quad + 1/2 (H_{2200}^{\circ} - H_{298}^{\circ})_{\text{N}_2}, \\
&= -67.0 - (36.634) + 2(13.045) + 1/2(15.144), \\
&= -67.0 - 36.634 + 26.090 + 7.572, \\
\Delta H_{f298.15}^{\circ} &= -69.972 \text{ kcal gfw}^{-1}.
\end{aligned}$$

The data used to reduce the Cost and Wert data are estimated, and hence cannot be given too great a weight. However, there is seen to be an appreciable discrepancy between calorimetry and dissociation-pressure data. For the present purposes, it is believed that greater confidence can be placed in the corrected calorimetric value. Accordingly, this value; i. e.,  $\Delta H_{f298.15}^{\circ} = -60.5 \text{ kcal gfw}^{-1}$ , is utilized as the heat of formation of  $\text{Nb}_2\text{N}$ .

#### 4) Vaporization data

In addition to the Cost and Wert<sup>5</sup> work already discussed, Pemsler<sup>6,7</sup> has studied Nb-N alloys in the range of compositions from pure niobium to  $\text{Nb}_2\text{N}$ . For the temperature range 2280° to 2470°C, he found the partial molar enthalpy of dissociation to be 84 kcal/mole  $\text{N}_2$ ; and for 2170° to 2280°C, the value was 121 kcal/mole  $\text{N}_2$ . For the  $\text{Nb}_2\text{N}$  composition, an integral enthalpy of dissociation of 27.7 kcal/g atom; i. e., 83.1 kcal/mole was found at the melting point (~2420°C (2693°K)). The value is appreciably larger numerically than that obtained by Cost and Wert at 2200°K.

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## 16.4 Niobium Oxides

### Phase Diagram and General Information

A complete phase diagram for the niobium-oxygen system was not given by Hansen and Anderko.<sup>1</sup> They show only the results of a study of the solubility of oxygen in niobium for the temperature range 775 to 1100°C based on the work of Seybolt.<sup>2</sup> Hansen and Anderko do note that Brauer<sup>3</sup> has concluded that there are three compounds NbO, NbO<sub>2</sub>, and Nb<sub>2</sub>O<sub>5</sub>. NbO has a cubic structure (NaCl type with ordered vacancies;  $a = 4.211 \text{ \AA}$ ), and a limited homogeneity range. The dioxide, NbO<sub>2</sub>, has no appreciable homogeneity range with a lattice only partly related to that of rutile. For Nb<sub>2</sub>O<sub>5</sub>, whose composition ranges down to Nb<sub>2</sub>O<sub>4.8</sub>, a melting point of 1460°C (1733 °K) has been observed by Brauer.<sup>3</sup> Hansen and Anderko<sup>1</sup> indicate that the three polymorphic forms of Nb<sub>2</sub>O<sub>5</sub> are not yet known. A report by Holser<sup>4</sup> indicates that the low-temperature  $\gamma$ -form of Nb<sub>2</sub>O<sub>5</sub> is orthorhombic with  $a = 6.19 \text{ \AA}$ ,  $b = 3.65 \text{ \AA}$ , and  $c = 3.94 \text{ \AA}$ .

Sisco and Epremian<sup>5</sup> (p. 599) mention the compounds Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub>, and suggest the possibility of NbO and Nb<sub>2</sub>O. Norman,<sup>6</sup> from oxidation studies of niobium, found two (NbO<sub>x</sub> and NbO<sub>z</sub>) tetragonal niobium suboxides. For one of these, he suggested the formula NbO<sub>0.5</sub> (Nb<sub>2</sub>O). However, attempts to prepare this suboxide (Nb<sub>2</sub>O) by argon-arc-melting of Nb-Nb<sub>2</sub>O<sub>5</sub> mixtures always led to formation of Nb and NbO. Further metallographic work by Norman *et al*<sup>7</sup> showed that NbO<sub>x</sub> could not be distinguished from the metal phase. The suboxides NbO<sub>z</sub> formed platelets in the metal.

Additional work on the suboxides has been reported by Brauer *et al*<sup>8</sup>, who proposed the formula Nb<sub>6</sub>O. Earlier, Brauer and Müller<sup>9</sup> had reported a suboxide of probable formula Nb<sub>2</sub>O being formed by oxidation of niobium, at 300°C. They were also able to synthesize this oxide by reaction of Nb and Nb<sub>2</sub>O<sub>5</sub>.

Miller<sup>10</sup> (p. 611) has given a fairly comprehensive review of the niobium oxides. For Nb<sub>2</sub>O<sub>5</sub>, the three crystalline forms were designated as L (low), M (middle) and H (high) by Brauer.<sup>3</sup> The L form was obtained by heating to 500°C. The M form appeared at 1000°C and the H form at 1100°C. The changes were not reversible. Additional details of the polymorphs of Nb<sub>2</sub>O<sub>5</sub> are discussed in the section devoted to Nb<sub>2</sub>O<sub>5</sub>.

One of the most comprehensive studies of the Nb-O system has been reported by Elliott,<sup>11</sup> who shows a phase diagram. This diagram does not show any niobium suboxides below NbO. Elliott indicated that NbO has a melting point of 3533°F (1945°C) and a lattice constant of 4.210 Å. NbO<sub>2</sub> has a melting point of 3479°F (1915°C) with a rutile structure.

A eutectic between Nb and NbO occurs at 3479 °F (1915°C) and another eutectic between NbO and NbO<sub>2</sub> occurs at 3290 °F (1810 °C). A peritectic reaction is believed to occur at 2750 °F (1510°C) between NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. Elliott considers Nb<sub>2</sub>O<sub>5</sub> to exist as a single form corresponding to the high-temperature modification already discussed.

Kolchin and Sumarokova<sup>12</sup> reported melting points of 1935 °C for NbO and 2080 °C for NbO<sub>2</sub>. They also reported vaporization data for NbO and NbO<sub>2</sub>.

Shveikin and Gel'd<sup>13</sup> made an X-ray study of niobium oxides formed by reduction of Nb<sub>2</sub>O<sub>5</sub> with Nb and C at 1200 to 1650 °C. They reported the existence of Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub>, NbO, and Nb. They could not find Nb<sub>2</sub>O, Nb<sub>4</sub>O, Nb<sub>3</sub>O<sub>7</sub>, Nb<sub>3</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>3</sub>, or Nb<sub>3</sub>O<sub>4</sub>.

Hurlen<sup>14</sup> has reported the formation of two niobium suboxides (NbO<sub>x</sub> and NbO<sub>y</sub>) in addition to NbO and NbO<sub>2</sub>. Brewer<sup>15</sup> had reviewed data for the niobium oxides available up to 1952. An early report of Nb<sub>2</sub>O was shown to be Nb<sub>2</sub>N. Pemsler<sup>16</sup> has studied the oxygen pressure over niobium-oxygen alloys. He noticed a second phase appearing at 7 atom-percent oxygen and assumed it to be NbO.

In reviewing the available data for the Nb-O system it appears that there are still considerable uncertainties in the types of compounds formed, especially in view of the large amount of research devoted to these materials in recent years. It appears that phases of Nb<sub>2</sub>O<sub>5</sub>, NbO<sub>2</sub> and NbO are sufficiently well characterized to permit thermodynamic table preparation. The data for the suboxides below NbO appear unsuitable for table preparation at the present time.

#### Supplement

Terao<sup>17</sup> has discussed the structure of the niobium oxides.

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#### 16.4.1 Niobium Monoxide (NbO<sub>(s, l)</sub>)

##### a. Crystal Structure and Melting Point

Brauer<sup>1</sup> has concluded that NbO has a cubic structure (NaCl type with ordered vacancies) and a lattice parameter,  $a = 4.211 \text{ \AA}$ . The compound has a limited homogeneity range. According to Miller<sup>2</sup> (p. 612), the NbO lattice is derived from a NaCl lattice by removing molecules so that 75 percent of the lattice positions are occupied, and the unoccupied ones are distributed in an ordered manner. Kusenko and Gel'd<sup>3</sup> have also noted that NbO has a cubic (NaCl type) lattice with  $a = 4.201 \text{ kX}$ . Additional work on the structure of NbO has been given by Elliott<sup>4</sup>, Anderson and Magneli<sup>5</sup> and Brauer and Morawietz.<sup>6</sup>

Melting points of 1935°C (2208°K) by Kolchin and Sumarokova<sup>7</sup> and 1945°C (2218°K) by Elliott<sup>4</sup> have been reported. The higher value of Elliott is accepted here.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

Kelley and King<sup>8</sup> do not list any experimental values of  $S_{298.15}^{\circ}$  for NbO. Kubaschewski and Evans<sup>9</sup> list an estimated value of  $11.5 \pm 1.5$  e. u. Brewer<sup>10</sup> gives an estimate of  $\Delta S_{298}^{\circ} = -22$  e. u. for the reaction  $\text{Nb} + 1/2 \text{O}_2 \longrightarrow \text{NbO}$ . Using  $S_{298.15}^{\circ}$ , Nb = 8.58 and  $1/2 S_{298.15}^{\circ}$ , O<sub>2</sub> = 24.503 e.u. it is found that  $S_{298.15}^{\circ}$ , NbO = 11.083 eu. Lavrent'ev et al<sup>11</sup> from emf equilibrium data found that  $\Delta S^{\circ} = -20.19$  eu. for the same reaction used by Brewer above, so that  $S_{298.15}^{\circ} = 12.893$  eu. Kusenko and Gel'd<sup>12</sup> have listed a value of  $S_{298.15}^{\circ} = 12.0$  eu. This is probably an estimate.

For the present calculations, it appears that the value of Lavrent'ev et al<sup>11</sup> may be rather large in view of the fact that the entropy value for NbO<sub>2</sub> is only 13.03 eu. Accordingly, the intermediate value of 12.0 eu. estimated by Kusenko and Gel'd<sup>12</sup> is used. This is in reasonable agreement with a value of 12.7 eu. estimated by the Latimer technique. A value of  $H_{298}^{\circ} - H_0^{\circ} = 1.800 \pm 0.200$  kcal gfw<sup>-1</sup> is estimated by comparison with the known values for Nb<sub>2</sub>O<sub>5</sub>, Nb, and NbO<sub>2</sub> already evaluated on this project. This estimate may not be completely compatible with the  $S_{298.15}^{\circ}$  value, but it is reasonable.

### 2) High-temperature heat content

Gel'd and Kusenko<sup>13</sup> have made high-temperature heat capacity measurements. They found:

$$C_p^{\circ} = 10.04 + 2.35 \times 10^{-3} T - 0.783 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Their equation is extrapolated to the adopted melting point of 2218°K.

The heat of fusion is estimated by assuming the entropy of fusion to be 6 eu. thus giving 13,000 cal gfw as the rounded heat of fusion at 2218°K.

Above the melting temperature, it is assumed that the heat capacity is constant and equal to 15.0 cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

### 3) Heat of formation

Calorimetric results via combustion of NbO to form Nb<sub>2</sub>O<sub>5</sub> by Kusenko and Gel'd<sup>3</sup> yielded a heat of formation,  $\Delta H_{f298.15}^\circ = -97.7 \pm 2.6$  kcal/gfw assuming a heat of formation of Nb<sub>2</sub>O<sub>5</sub> of -458.6 kcal/gfw. Using our presently selected value of -454.6 kcal/gfw for Nb<sub>2</sub>O<sub>5</sub>, we then find that the heat of formation at 298.15°K for NbO is -95.70 kcal/gfw. Morozova and Getskina<sup>14</sup> used a heat of formation of  $-472.6 \pm 1.0$  kcal/gfw for Nb<sub>2</sub>O<sub>5</sub> to derive a heat of formation of  $-108.8 \pm 0.6$  kcal/gfw for NbO. Using our selected value for Nb<sub>2</sub>O<sub>5</sub> we then find that for NbO, the heat of formation is  $\Delta H_{f298.15}^\circ = -99.8$  kcal/gfw. It can be noted that Morozova and Stolyarova<sup>15</sup> had recorrected their data to -99.9 kcal/gfw assuming that  $\Delta H_{fNb_2O_5}^\circ = -454.8$  kcal/gfw which is consistent with our correction.

Lavrent'ev et al<sup>11</sup> from emf measurements found that  $\Delta H_{fNbO, 298.15^\circ K}^\circ = -98.39$  kcal/gfw.

Brewer<sup>10</sup> reviewed the data of Grube, Kubaschewski and Zwiauer<sup>16</sup> and found that  $\Delta H_{fNbO, 298.15}^\circ = -97 \pm 2$  kcal/gfw.

The results of the two calorimetric and the two equilibrium determinations can now be summarized:

$\Delta H_{f298.15}^\circ$ kcal/gfw	Reference
-95.70	Recalc. of Kusenko and Gel'd <sup>3</sup>
-99.8	Recalc. of Morozova and Getskina <sup>14</sup>
-98.39	Lavrent'ev et al <sup>11</sup>
-97.0	Brewer <sup>10</sup>

Average  $\Delta H_{f298.15}^\circ = -97.72$  kcal gfw<sup>-1</sup>

For the present tabulation the average rounded value of  $-97.7 \pm 2.0$  kcal/gfw is accepted as the heat of formation of NbO at 298.15°K.

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## 16. 4. 2 Niobium Monoxide (NbO<sub>(g)</sub>)

### a. Thermodynamic Functions

*Spectroscopic work on the NbO molecule appears to have been first published in 1950. V. R. Rao<sup>1</sup> studied the emission spectrum of NbO and noted three band systems as shown in table 39.*

TABLE 39  
BAND SYSTEMS OBSERVED BY RAO<sup>1</sup>

System	Wavelength Region (Å)	Probable Transition
A	4200-5100	$4\Pi \leftrightarrow 4\Pi$
B	5100-6100	$4\Sigma \leftrightarrow 4\Pi$
C	6100-infrared	$4\Sigma \leftrightarrow 4\Pi$

His observations indicated that the lower state of all three systems was probably the ground state. The following states of the NbO molecules were thus indicated. (See table 40.)

TABLE 40  
SUMMARY OF STATES OBSERVED BY RAO<sup>1</sup>

State	$\nu_e$ (cm <sup>-1</sup> )	$\omega_e$ (cm <sup>-1</sup> )	$x_e \omega_e$ (cm <sup>-1</sup> )
A $4\Pi$	21400	855.2	3.9
B $4\Sigma$	18280	998	16.
C $4\Sigma$	16260	992	7.5
X $4\Pi$	0	~ 1000	6.5

V. R. Rao and Premaswarup<sup>2</sup> subsequently studied system C and could not be definite about the electronic transition involved, although the  $4\Sigma - 4\Pi$  transition is a strong possibility. Their analysis yielded

$$\nu = \left. \begin{array}{l} 15484.1 \\ 15431.3 \\ 15244.9 \\ 14880.6 \end{array} \right\} + 919.5(\nu' + 1/2) - 20.3(\nu' + 1/2)^2 - 996.0(\nu'' + 1/2) + 9.0(\nu'' + 1/2)^2.$$

K. S. Rao<sup>3</sup> published a rotational analysis for system A in which an error for  $r_e$  was introduced. He revised this work in subsequent publications<sup>4, 5</sup> and tabulated the values shown in table 41. No definite interpretation of electronic transitions was mentioned, but an analogy to the VO molecule which has a  ${}^2\Delta - {}^2\Delta$  transition is mentioned.

TABLE 41

ROTATIONAL CONSTANTS FROM RAO<sup>4, 5</sup> FOR SYSTEM A

	$B_e$ (cm <sup>-1</sup> )	$a_e$ (cm <sup>-1</sup> )	$r_e$ (Å)	$I_e$ (gm-cm <sup>2</sup> )
Upper State	0.3461	0.0027	1.889	$80.852 \times 10^{-40}$
Lower State	0.3791	0.0030	1.805	$73.814 \times 10^{-40}$

K. S. Rao<sup>6</sup> has reported additional studies of system A and indicates that this most likely corresponds to a  ${}^4\Sigma - {}^4\Sigma$  transition.

On the other hand, Uhler<sup>7, 8</sup> has made vibrational and rotational analyses of system A which give results differing from the erroneous one of Rao<sup>3</sup> (1952) and the later ones by Rao<sup>4, 5, 6</sup>. Uhler has considered the transition to be  $A {}^2\Delta - X {}^2\Delta$  and found the constants tabulated in table 42. The internuclear distance for the ground state is  $r_e = 1.691$  Å.

TABLE 42

VIBRATIONAL AND ROTATIONAL CONSTANTS BY UHLER<sup>7, 8</sup>  
(Units are cm<sup>-1</sup>)

State	$\nu_e$	$\omega_e$	$x_e \omega_e$	$B_e$	$a_e$	$D_e$
A ${}^2\Delta$	21385.3	850.4 <sub>8</sub>	3.37	0.4003	0.0020	$3.0 \times 10^{-7}$
X ${}^2\Delta$	0	989.0 <sub>3</sub>	3.8 <sub>3</sub>	0.4323	0.0024	$2.6 \times 10^{-7}$

From the available data, we select the Uhler<sup>7, 8</sup> data to represent the ground state and excited state A, and accept the data from Rao<sup>1</sup> for the excited states B, and from Rao and Premaswarup<sup>2</sup> for state C. The final selected values are shown in table 43. The electronic energy value for the C state was taken as the intermediate rounded value of 15,400 cm<sup>-1</sup>. Values of B<sub>e</sub> were estimated for states B and C to be equal to 0.41 cm<sup>-1</sup> by comparison with states X and A. To remain consistent with the Uhler<sup>7, 8</sup> interpretation of doublet systems, we have assigned degeneracy values of 4 to states B and C.

TABLE 43

SELECTED SPECTROSCOPIC CONSTANTS USED FOR NbO<sub>(gas)</sub>

State	g	E	$\omega_e$	$\omega_e x_e$	B <sub>e</sub>	$\alpha_e$	D <sub>e</sub>
		cm <sup>-1</sup>					
X <sup>2</sup> $\Delta$	4	0.0	989.03	3.83	0.4323	0.0024	2.6 x 10 <sup>-7</sup>
C	4	15,400	919.5	20.3	0.41	--	--
B	4	18,280	998.	16.0	0.41	--	--
A <sup>2</sup> $\Delta$	4	21,385.3	850.48	3.37	0.4003	0.0020	3.0 x 10 <sup>-7</sup>

In the computations made using these data, it is clear that there may be appreciable uncertainties because of the possibility of other low-lying electronic states.

To investigate the possible errors to which the data for NbO<sub>(g)</sub> might be subject, several additional computations were carried out. The various types of input data used are shown in table 44. The results obtained are shown in table 45.

The results obtained in table 45 show that the biggest effect is occasioned by different choices of electronic states. Thus, the differences between HS-74 and HS-88 probably give an indication of the uncertainties in the data. The data for HS-95 checked the data for HS-88, as was to be expected utilizing two different computer programs. Similarly, the data for HS-94 also obtained on the polyatomic gas computer program checked the data for HS-93 via the diatomic gas computer program. For case HS-96, an effort was made to reproduce the calculations of Brewer and Chandrasekharaiah<sup>9</sup> (UCRL8713). It can be

TABLE 44

INPUT DATA USED FOR VARIOUS CASES FOR  $\text{NbO}(\text{g})$ 

Case HS-74--These data are shown in table 43 and are used in the present report.								
Case HS-88--This case uses electronic energy levels for Nb <sup>2+</sup> .								
$\omega_e$ (cm <sup>-1</sup> )	989.03	989.03	989.03	989.03	989.03	989.03	989.03	989.03
$B_e$ (cm <sup>-1</sup> )	0.4323	0.4323	0.4323	0.4323	0.4323	0.4323	0.4323	0.4323
E (cm <sup>-1</sup> )	0.0	516.9	1176.6	1939.3	25221.2	25736.5	26464.9	27374
g	4	6	8	10	4	6	8	10
Case HS-92--Same as HS-74, except no second-order terms.								
$\omega_e$ (cm <sup>-1</sup> )	989.03	919.5	998.	850.48				
$B_e$ (cm <sup>-1</sup> )	0.4323	0.41	0.41	0.4003				
E (cm <sup>-1</sup> )	0.0	15400.	18280.	21385.3				
g	4	4	4	4				
Case HS-93--Use same electronic levels as for HS-74. However use only a constant $\omega_e$ and $B_e$ .								
$\omega_e$ (cm <sup>-1</sup> )	989.03	989.03	989.03	989.03				
$B_e$ (cm <sup>-1</sup> )	0.4323	0.4323	0.4323	0.4323				
E (cm <sup>-1</sup> )	0.0	15400	18280	21385.3				
g	4	4	4	4				
Case HS-94--Used identical data as in HS-93, but was computed on the polyatomic gas computer program, whereas case HS-93 had utilized the diatomic gas program.								
Case HS-95--Used identical data as for HS-88, but was computed on the polyatomic gas computer program, whereas Case HS-88 had utilized the diatomic gas program.								
Case HS-96--Uses same data as UCRL-8713								
$\omega_e$ (cm <sup>-1</sup> )	838	838	838	838	838	838	838	838
$B_e$ (cm <sup>-1</sup> )	0.4323	0.4323	0.4323	0.4323	0.4323	0.4323	0.4323	0.4323
E (cm <sup>-1</sup> )	0.0	516.9	1176.6	1939.3	25221.2	25736.5	26464.9	27374.7
g	4	6	8	10	4	6	8	10



TABLE 45

OUTPUT DATA FOR NbO(g) FOR VARIOUS CASES

T (°K)	Case	C <sub>p</sub> <sup>°</sup>	S <sub>T</sub> <sup>°</sup>	$-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)$	H <sub>T</sub> <sup>°</sup> - H <sub>298.15</sub> <sup>°</sup>
		(cal deg K <sup>-1</sup> gfw <sup>-1</sup> )			(kcal gfw <sup>-1</sup> )
298.15	HS-74	7.358	57.091	57.091	0.0
	88	8.929	57.938	57.938	0.0
	92	7.345	57.079	57.079	0.0
	93	7.345	57.079	57.079	0.0
	94	7.345	57.079	57.079	0.0
	95	8.929	57.938	57.938	0.0
	96	9.130	58.019	58.019	0.0
	UCRL-8713			~ 57.81	
1000	HS-74	8.688	66.890	61.113	5.777
	88	9.995	69.849	62.870	6.979
	92	8.639	66.844	61.089	5.755
	93	8.639	66.844	61.089	5.755
	94	8.639	66.844	61.089	5.755
	95	9.995	69.849	62.870	6.979
	96	10.074	70.135	63.048	7.067
	UCRL-8713			~ 63.099	
2000	HS-74	8.963	73.018	65.701	14.634
	88	9.343	76.539	68.243	16.592
	92	8.866	72.925	65.655	14.541
	93	8.865	72.925	65.655	14.541
	94	8.865	72.925	65.655	14.541
	95	9.343	76.539	68.243	16.592
	96	9.366	76.856	68.485	16.743
3000	HS-74	9.177	76.688	68.791	23.690
	88	9.135	80.280	71.676	25.812
	92	9.015	76.544	68.720	23.469
	93	9.004	76.542	68.720	23.465
	94	9.004	76.542	68.720	23.465
	95	9.135	80.280	71.676	25.812
	96	9.145	80.604	71.945	25.978
	UCRL-8713			~ 71.966	

TABLE 45 (Concl'd)

T (°K)	Case	$C_p^\circ$	$S_T^\circ$	$-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)$	$H_T^\circ - H_{298.15}^\circ$
		(cal deg K <sup>-1</sup> gfw <sup>-1</sup> )			(kcal gfw <sup>-1</sup> )
4000	HS-74	9.661	79.388	71.118	33.082
	88	9.070	82.897	74.170	34.907
	92	9.377	79.181	71.020	32.645
	93	9.330	79.172	71.018	32.615
	94	9.330	79.172	71.018	32.615
	95	9.070	82.897	74.170	34.907
	96	9.076	83.223	74.453	35.080
5000	HS-74	10.413	81.623	73.003	43.102
	88	9.085	84.921	76.125	43.978
	92	9.908	81.329	72.873	42.281
	93	9.805	81.304	72.868	42.176
	94	9.805	81.304	72.868	42.176
	95	9.085	84.921	76.125	43.978
	96	9.089	85.248	76.417	44.157
6000	HS-74	11.269	83.601	76.611	53.939
	88	9.160	86.583	77.734	53.097
	92	10.432	83.183	74.440	52.458
	93	10.277	83.134	74.430	52.224
	94	10.277	83.134	74.430	52.224
	95	9.160	86.583	77.734	53.097
	96	9.163	86.911	78.031	53.278

LEGEND FOR TABLE 45

HS-74--Case used in present report; observed electronic states are utilized.

HS-88 } Both cases use same data;  $\omega_e = 989.03 \text{ cm}^{-1}$ ;  $B_e = 0.4323 \text{ cm}^{-1}$  and  
HS-95 } first eight electronic levels for  $\text{Nb}^{+2}$ . Case HS-88 was calculated on  
diatomic gas computer program; case HS-95 was calculated on  
polyatomic gas computer program.

HS-92--Same as HS-74 except no anharmonic terms are included.

HS-93 } Both cases use same data as for HS-92 except  $\omega_e = 989.03 \text{ cm}^{-1}$  entirely.  
HS-94 } Case HS-93 was calculated by diatomic gas program; case HS-94 was  
calculated by polyatomic gas program.

HS-96--Input data the same as used by Brewer and Chandrasekharaiah (UCRL-8713)<sup>9</sup>.

UCRL-8713--Data reported by Brewer and Chandrasekharaiah.<sup>9</sup>

seen that the agreement with their data is satisfactory. Case HS-92 can be compared with HS-74 which shows that neglect of second-order terms leads to relatively small changes in the thermodynamic functions up to 6000 °K.

b. Heat of Formation

Ackermann and Thorn<sup>10</sup> have noted that there are no vaporization data for niobium oxides. For the related Ta-O system, they have favored a lower heat of dissociation of  $8.4 \pm 0.5$  ev for TaO and  $15.0 \pm 0.5$  ev for TaO<sub>2</sub>. For VO<sub>(g)</sub> a heat of dissociation of 6.4 ev is indicated. Other heats of dissociation which they give are listed below.

SOME HEATS OF DISSOCIATION FROM ACKERMANN AND THORN<sup>10</sup>

Molecule	Heat of Dissociation (ev)
TaO	$8.4 \pm 0.5$
TaO <sub>2</sub>	$15.0 \pm 0.5$
VO	6.4
ZrO	$7.8 \pm 0.2$
ZrO <sub>2</sub>	$15.2 \pm 0.2$
HfO	$8.0 \pm 0.5$
TiO	$6.9 \pm 0.1$
CrO*	$4.5 \pm 0.3$

\*Calculated from data of present project; see tables 134, 135, and 180 of volume 2.

Here, if one compares the heats of dissociation of TiO and VO, one sees that TiO is more stable by 0.5 ev. Assuming the same difference to exist between ZrO and NbO, one calculates a heat of dissociation of NbO of  $7.8 - 0.5 = 7.3$  ev.

For  $\text{NbO}_2$ , Shchukarev et al<sup>11</sup> found a dissociation energy of  $14.9 \pm 0.1$  ev. If the ratio of  $\frac{D_{\text{NbO}}}{D_{\text{NbO}_2}} = \frac{D_{\text{TaO}}}{D_{\text{TaO}_2}}$  then we estimate a heat of dissocia-

tion for NbO of  $D_{\text{NbO}} = 8.3$  ev. If one uses the ratio  $\frac{D_{\text{NbO}}}{D_{\text{NbO}_2}} = \frac{D_{\text{ZrO}}}{D_{\text{ZrO}_2}}$

then one calculates  $D_{\text{NbO}} = \frac{7.8}{15.2} \times 14.9 = 7.64$  ev. If one assumes that

$D_{\text{NbO}} = 1/2 D_{\text{NbO}_2}$  it is found that  $D_{\text{NbO}} = 7.45$  ev.

In our analysis of  $\text{NbO}_2$ , we found that the Shchukarev et al,<sup>11</sup> data yielded dissociation energies of  $\text{NbO}_2$  of 14.422 ev. Then we calculate corresponding estimates for  $D_{\text{NbO}}$  of 8.09 ev, 7.5 ev, and 7.2 ev. It would appear that the lower values can be considered as lower limits for the dissociation energy. These simple estimates thus indicate that the dissociation energy of NbO is in the range 7.2 to 8.3 ev.

Shchukarev et al<sup>12</sup> (1959) had reported vaporization of  $\text{NbO}_{2(\text{solid})}$  from a platinum strip. They observed  $\text{NbO}^+$  ions in a ratio of 0.21 compared to unity for  $\text{NbO}_2^+$  ions. An effective heat corresponding to the formation of NbO was tabulated as  $\Delta H_{1500-1680^\circ\text{K}}^\circ = 140 \pm 5$  kcal/mole. However, the reaction involved was not identified and no further reduction of data was presented.

In more recent work, however, Shchukarev et al<sup>13</sup> have studied the vaporization of  $\text{NbO}_{0.98}$  in a mass spectrometer over the range 1500 to 1650°C (1773 to 1923°K). From a slope of the  $\log(I^+ T)$  versus  $1/T$  plot, they obtained a heat of sublimation of  $\text{NbO}_{(\text{g})}$  from  $\text{NbO}_{0.98}$  of  $138 \pm 3$  kcal/mole. Disregarding the small deviation from stoichiometry, it is possible to calculate the heat of formation of the  $\text{NbO}_{(\text{g})}$  at 298.15°K. For these calculations, we assume the heat of sublimation observed applies to 1880°K. Then

$$\begin{aligned} \Delta H_{f;\text{NbO}(\text{g}); 298.15}^\circ &= \Delta H_{\text{sub};1800}^\circ + (H_T^\circ - H_{298.15}^\circ)_{\text{NbO}(\text{solid})} - (H_T^\circ - H_{298.15}^\circ)_{\text{NbO}(\text{g})} \\ &+ \Delta H_{f;\text{NbO}(\text{solid}); 298.15^\circ\text{K}}^\circ \end{aligned}$$

$$\Delta H_f^\circ; \text{NbO}_{(g)}; 298.15 = 138 + 18.562 - 12.845 + (-97.700) \\ = 46.017 \text{ kcal/mole.}$$

This value of the heat of formation is accepted. It is considered to have an uncertainty of  $\pm 5$  kcal/mole.

Also, the heat of formation at 0°K is found as

$$\Delta H_f^\circ; \text{NbO}_{(g)}; 0^\circ\text{K} = \Delta H_f^\circ; 298 + (H_T^\circ - H_{298.15}^\circ)_{\text{Nb}} + 1/2 (H_T^\circ - H_{298.15}^\circ)_{\text{O}_2} \\ - (H_T^\circ - H_{298.15}^\circ)_{\text{NbO}_{(g)}} \\ = 46.017 + 1.264 + 1.037 - 2.099$$

$$\Delta H_f^\circ; \text{NbO}_{(g)}; 0^\circ\text{K} = 46.219 \text{ kcal/mole}$$

Furthermore, the heat of dissociation at 0°K becomes

$$\Delta H_{\text{Diss}}^\circ; 0^\circ\text{K} = 171.103 + 58.986 - 46.219 \\ = 183.870 \text{ kcal/mole}$$

$$\Delta H_{\text{Diss}}^\circ; 0^\circ\text{K} = 7.972 \pm 0.2 \text{ ev.}$$

This value is compatible with the estimates made earlier in this section. In making the above calculations and conversions, data obtained earlier and currently on this project have been utilized.

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### 16.4.3 Niobium Dioxide ( $\text{NbO}_{2(s,l)}$ )

#### a. Crystal Structure and Melting Points

As indicated in the general discussion, Brauer<sup>1</sup> found  $\text{NbO}_2$  to have no appreciable homogeneity range with a lattice related to that of a tetragonal rutile. He reported  $a = 4.84 \text{ \AA}$ , and  $c = 2.99 \text{ \AA}$ , and  $c/a = 0.618$ . King and Christensen<sup>2</sup> reported heat content measurements which indicated anomalies at 1090 and 1200°K. They interpreted their data to give three forms of  $\text{NbO}_2$ . The low temperature form is  $\alpha\text{-NbO}_2$ , the intermediate form is  $\beta\text{-NbO}_2$ , and the high temperature form is  $\gamma\text{-NbO}_2$ . Gel'd and Kusenko<sup>3</sup> reported a single transition at 1040°K, Kusenko and Gel'd<sup>4</sup> found that for  $\text{NbO}_2$ ,  $a = 4.82 \text{ kX}$  and  $c = 2.99 \text{ kX}$ . Marinder<sup>5</sup> has made a comprehensive study of the crystal structure of  $\text{NbO}_2$ . He shows that the crystal is built of  $\text{NbO}_6$  octahedra joined at the edges and corners as in the rutile structure. The Nb-Nb distances are alternately 2.8 and 3.20 Å; the Nb-O distances are 2.0-2.1 Å, and the O-O distances are 2.6-3.0 Å.

Melting points of 2080°C (2353°K) by Kolchin and Sumarokova<sup>6</sup> and 1915°C (2168°K), by Elliott<sup>7</sup> have been reported. The average is 2270°K, which is accepted here. Elliott<sup>7</sup> did not report any phase transitions.

At the present time, it is clear that all the details regarding structure and ranges of stability for  $\text{NbO}_2$  are not yet definite, since there appears to be no information regarding the forms of  $\text{NbO}_2$  produced at 1090 and 1200°K.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at 298.15°K

Kelley<sup>8</sup> lists a single experimental determination of the entropy at 298.15°K for  $\text{NbO}_2$ . It is based on the work of King<sup>9</sup> for the temperature range 51 to 297°K. and yields  $S_{298.15}^\circ = 13.03 \pm 0.07 \text{ eu.}$  with  $C_{p,298.15}^\circ = 13.74 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Lavrent'ev et al<sup>10</sup> from equilibrium studies of niobium oxides found that for the reaction  $\text{Nb} + \text{O}_2 \rightarrow \text{NbO}_2$  that  $\Delta S_{298.15}^\circ = -45.76 \text{ eu.}$  Using  $S_{298.15}^\circ$  values of 8.58 eu. for Nb from Clusius et al<sup>11</sup> and 49.007 eu. for  $\text{O}_2$  from Barriault et al<sup>12\*</sup> we calculate that  $S_{298.15}^\circ = 11.827 \text{ eu.}$  for  $\text{NbO}_2$ . Coughlin<sup>13</sup> found  $S_{298.15}^\circ = 14.85 \text{ eu.}$  from the equilibrium data of Sue.<sup>14</sup> These latter values deviate somewhat compared to the direct experimental determination which we prefer for the present calculations. A value of  $H_{298.15}^\circ - H_0^\circ = 2.222 \text{ kcal/gfw}$  was calculated here from the experimental data of King.<sup>9</sup>

\*See also volume 2, present report (table 197).



## 2) High-temperature heat content

King and Christensen<sup>2</sup> and Gel'd and Kusenko<sup>3</sup> have reported high-temperature heat content data for NbO<sub>2</sub>. King and Christensen<sup>2</sup> reported two heat content anomalies at 1090 and 1200°K. They state that no isothermal heat absorption is associated with either anomaly. However, in their final interpretation they have considered NbO<sub>2</sub> to exist in three forms with an associated heat of transition at 1090°K.

$$C_p^\circ = 11.70 + 9.56 \times 10^{-3} T - 0.72 \times 10^5 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

for  $\alpha$ -NbO<sub>2</sub> from 298.15 to 1090°K

$$\Delta H_{1090}^\circ = 720 \text{ calories/gfw}$$

$$C_p^\circ = 22.20 \text{ cal deg K}^{-1} \text{ gfw}^{-1} \text{ for } \beta\text{-NbO}_2 \text{ from 1090 to 1200°K}$$

$$C_p^\circ = 19.85 \text{ cal deg K}^{-1} \text{ gfw}^{-1} \text{ for } \gamma\text{-NbO}_2 \text{ from 1200 to 1800°K.}$$

Gel'd and Kusenko<sup>3</sup> reported a transition at 1040°K with an associated heat of transition of 700 cal/gfw in good agreement with King and Christensen. Gel'd and Kusenko<sup>3</sup> represented their data by

$$C_p^\circ = 14.681 + 6.156 \times 10^{-3} T - 2.421 \times 10^5 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

for the range 298.15 to 1040°K,

and  $C_p^\circ = 21.28 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  above 1040°K.

Gel'd and Kusenko did not mention a second anomaly at 1200°K as did King and Christensen.<sup>2</sup>

For the present purposes, we accept the King and Christensen data for the entire temperature range of their experiments. Their value of heat capacity up to 1800°K was extrapolated to the melting point. The heat of fusion was estimated by using the entropy

of fusion for NbO<sub>2.5</sub> from Orr,<sup>15</sup>  $\Delta S_f^\circ = \frac{24590}{2 \times 1785} = 6.887 \text{ eu.}$

Therefore, the heat of fusion becomes  $2270^\circ\text{K} \times 6.887 = 15633 \text{ cal/gfw}^{-1}$ , which is rounded off to  $15,000 \pm 5000 \text{ cal/gfw.}$

Above the melting point, the heat capacity of liquid NbO<sub>2</sub> was estimated to be 20.0 cal deg K<sup>-1</sup>gfw<sup>-1</sup>.

### 3) Heat of formation

In their original calorimetric work, Morozova and Getskina<sup>16</sup> reported data for the combustion of NbO<sub>2</sub> which they (Morozova and Stolyarova)<sup>17</sup> later corrected because of an incorrect heat of combustion of metallic niobium. Using the value of  $\Delta H_{f,Nb_2O_5,298.15}^\circ = -454.8$  kcal/gfw, they find that  $\Delta H_{f,NbO_2,298.15}^\circ = -190.4 \pm 0.4$  kcal/gfw. This value is not altered significantly by using our accepted value for the heat of formation of Nb<sub>2</sub>O<sub>5</sub>, i.e., -454.6 kcal/gfw, which leads to  $\Delta H_{f,NbO_2,298.15}^\circ = -190.3 \pm 0.4$  kcal/gfw. Kusenko and Gel'd<sup>4</sup> used a value of -458.6 kcal/gfw for Nb<sub>2</sub>O<sub>5</sub> to derive  $-191.7 \pm 2.6$  kcal/gfw for the heat of formation of NbO<sub>2</sub>. If we correct their data using our value of -454.6 kcal/gfw for Nb<sub>2</sub>O<sub>5</sub>, we obtain  $\Delta H_{f,298.15,NbO_2}^\circ = -189.7$  kcal/gfw. Mah<sup>18</sup> found by oxygen combustion that  $\Delta H_{f,298.15,NbO_2}^\circ = -190.9 \pm 0.4$  kcal/gfw using  $\Delta H_{f,298.15,Nb_2O_5}^\circ = -455.2$  kcal/gfw. Correcting to be consistent with our value of -454.6, we obtain  $-190.6 \pm 0.4$  kcal/gfw as the heat of formation of NbO<sub>2</sub> at 298.15°K. Summarized below are the three values obtained calorimetrically:

$\Delta H_{f,298.15}^\circ$ kcal/gfw	Original Reference
-190.3	Morozova and Stolyarova <sup>17</sup>
-189.7	Kusenko and Gel'd <sup>4</sup>
-190.6	Mah <sup>18</sup>

average  $\Delta H_{f,298.15}^\circ = -190.2$  kcal/gfw.

In addition to the calorimetric values, Lavrent'ev *et al*<sup>10</sup> from equilibrium studies found that  $\Delta H_{f,298.15,NbO_2}^\circ = -193.3$  kcal/gfw and Brewer<sup>19</sup> in reviewing earlier equilibrium data found  $\Delta H_{f,298.15,NbO_2}^\circ = -189.0 \pm 1.0$  kcal/gfw.

For the present purposes, we accept the average of the calorimetric data, i.e.,  $\Delta H_{f,298.15,NbO_2}^\circ = -190.2 \pm 1.0$  kcal/gfw. The uncertainty given here is estimated by comparison with the data thus far reported.

#### 4) Vaporization studies

Shchukarev et al<sup>20</sup> studied the vaporization of NbO<sub>2</sub> from a molybdenum Knudsen cell. They found the heat of dissociation of NbO<sub>2</sub> (gas) to be  $14.9 \pm 0.1$  ev (343.638 kcal/gfw). Earlier Shchukarev et al<sup>21</sup> had vaporized NbO<sub>2</sub> from a platinum strip and obtained a heat of dissociation of NbO<sub>2</sub> (gas) of  $14.8 \pm 0.5$  ev. Other vaporization data have been given by Shchukarev et al<sup>22</sup> more recently. Brewer and Rosenblatt<sup>23</sup> estimated the dissociation energy of NbO<sub>2</sub>(g) to be  $320 \pm 25$  kcal/gfw.

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#### 16.4.4 Niobium Dioxide (NbO<sub>2</sub>(g))

##### a. Thermodynamic Functions

There are no known reported spectroscopic studies for the spectroscopic constants of NbO<sub>2</sub>(g). Approximate thermodynamic functions can be obtained by suitable estimates of the spectroscopic constants however. Chandrasekharaiah and Brewer<sup>1</sup> obtained free energy functions at 500 °K intervals from 1000 to 3000 °K for NbO<sub>2</sub> by assuming the molecule to be linear with vibrational frequencies of 870, 262 (mult = 2), and 1009 cm<sup>-1</sup>. Additional data have been given by Brewer and Rosenblatt.<sup>2</sup> They assumed the stretching force constant of the dioxide to be the same as the monoxide. They utilized the internuclear distance (1.691 Å) from the corresponding monoxide as tabulated by Sutton.<sup>3</sup> However, the vibrational frequency used by Brewer and Rosenblatt<sup>2</sup> is  $\omega = 942 \text{ cm}^{-1}$ . The internuclear distance is consistent with the data of Uhler,<sup>4, 5</sup> but the vibrational frequency is lower than their value of 989.03 cm<sup>-1</sup>. We have used the latter value and the valence bond theory as used by Chandrasekharaiah and Brewer<sup>1</sup> and elsewhere on this project to obtain the frequencies 913.6 cm<sup>-1</sup>, 276.2 cm<sup>-1</sup> (mult = 2), and 1059.2 cm<sup>-1</sup>. The moment of inertia was  $15.1918 \times 10^{-39} \text{ gm cm}^2$  and  $B_e = 0.18424 \text{ cm}^{-1}$ . To estimate electronic contributions, an ionic model has been assumed as suggested by Brewer and Rosenblatt.<sup>2</sup> Energy levels tabulated by Moore<sup>6</sup> for Nb<sup>+4</sup> were used.

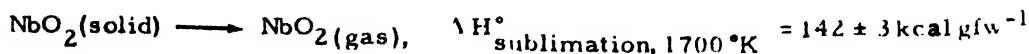
To illustrate the effects of different choices of input data to the polyatomic gas program, several additional calculations were made for NbO<sub>2</sub>(g). In table 46 are summarized the input data tried. It can be noted that the data for case HS-80 correspond to the data accepted. Some of the results obtained are compared in table 47. The variations in data are considered to give an indication of the uncertainties to which the selected data are subject.

##### b. Heat of Formation

Vaporization studies of NbO<sub>2</sub>(g) from NbO<sub>2</sub> were reported by Shchukarev et al.<sup>7</sup> They used a platinum strip to vaporize the NbO<sub>2</sub> in a mass spectrometer at temperatures of 1500 to 1880 °K. By a second-law method of plotting  $\log(I^\dagger T)$  versus  $\frac{1}{T}$ , they found

$$\Delta H_{\text{sublimation}}^\circ = 142 \pm 3 \text{ kcal/mole.}$$

The reaction they studied is



Then, for the formation reaction, i.e.,

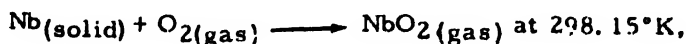


TABLE 46

SUMMARY OF NbO<sub>2</sub>(gas) INPUT DATA

Case HS-75	Using Data of Chandrasekharaiah and Brewer <sup>1</sup> (UCRL - 8736)			
$\omega(\text{cm}^{-1})$	870.	262.	262.	1009.
$E(\text{cm}^{-1})$	0.0	1870.		
$g$	4	6		
$\sigma$	2			
$B_e(\text{cm}^{-1})$	0.18423			
Case HS-77	(Same data as HS-75 except one electronic state with $g = 4$ )			
Case HS-79	(Use the 4- $\omega$ values calculated here; one electronic state with $g = 1$ )			
$\omega(\text{cm}^{-1})$	913.6	276.2	276.2	1059.2
$E(\text{cm}^{-1})$	0.0			
$g$	1			
$\sigma$	2			
$B_e(\text{cm}^{-1})$	0.18424			
Case HS-80*	(Same as HS-79 except electronic states and degeneracies are from Moore <sup>6</sup> )			
$\omega(\text{cm}^{-1})$	913.6	276.2	276.2	1059.2
$E(\text{cm}^{-1})$	0.0	1870.		
$g$	4	6		
$\sigma$	2			
$B_e(\text{cm}^{-1})$	0.18424			
Case HS-81*	(Same as HS-79 except assume single electronic ground state with $g = 4$ )			
$\omega(\text{cm}^{-1})$	913.6	276.2	276.2	1059.2
$E(\text{cm}^{-1})$	0.0			
$g$	4			
$\sigma$	2			
$B_e(\text{cm}^{-1})$	0.18424			

\*Data from Case HS-80 are used in the present work.

TABLE 47

COMPARISON OF CALCULATED DATA FOR  $\text{NbO}_2(\text{g})$   
(See Table 46 for Choice of Input Data)

Case	$C_p^\circ$ cal/deg K-gfw	$S^\circ$ cal/deg K gfw	$-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)$ cal/deg K gfw	$H_T^\circ - H_{298.15}^\circ$ kcal/mole
		Data at $T = 298.15^\circ\text{K}$		
HS-75	11.379	61.256	61.256	0.0
HS-77	11.350	61.252	61.252	0.0
*BR	--	--	61.3	--
HS-79	11.189	58.273	58.273	0.0
**HS-80	11.218	61.031	61.031	0.0
HS-81	11.189	61.028	61.028	0.0
Data at $T = 1000^\circ\text{K}$				
HS-75	15.508	77.765	67.889	9.875
HS-77	14.302	77.078	67.696	9.383
BR	--	--	67.9	--
HS-79	14.246	73.951	64.646	9.305
HS-80	15.452	77.392	67.594	9.798
HS-81	14.246	76.706	67.401	9.305
Data at $T = 2000^\circ\text{K}$				
HS-75	15.471	88.583	75.845	25.476
HS-77	14.744	87.176	75.189	23.975
BR	--	--	75.9	--
HS-79	14.728	84.026	72.092	23.867
HS-80	15.454	88.188	75.503	25.369
HS-81	14.728	86.781	74.847	23.867
Data at $T = 3000^\circ\text{K}$				
HS-75	15.209	94.800	81.200	40.801
HS-77	14.832	93.175	80.251	38.772
BR	--	--	81.2	--
HS-79	14.825	90.020	77.136	38.653
HS-80	15.201	94.400	80.839	40.682
HS-81	14.825	92.775	79.890	38.653

\*BR = Brewer and Rosenblatt, <sup>2</sup> Chem. Revs. 61, 257 (1961).

\*\*Case HS-80 is used in present report.

we have

$$\begin{aligned}
 \Delta H_{f; 298.15, \text{NbO}_2(\text{g})}^{\circ} &= \Delta H_{\text{sublimation; } 1700^{\circ}\text{K}}^{\circ} + (H_T^{\circ} - H_{298}^{\circ})_{\text{NbO}_2(\text{solid})} \\
 &\quad - (H_T^{\circ} - H_{298}^{\circ})_{\text{NbO}_2(\text{g})} + \Delta H_{f; \text{NbO}_2(\text{s}); 298.15}^{\circ} \\
 &= 142. + 27.430 - 20.717 - 190.2 \\
 &= -41.487 \text{ kcal/mole.}
 \end{aligned}$$

The data used in these conversions are tabulated in table 48 and originate from the present project. 8, 9

TABLE 48

PERTINENT DATA FROM PRESENT PROJECT  
USED IN CONVERSIONS

T(°K)	NbO(solid) $H_T^{\circ} - H_{298}^{\circ}$	NbO <sub>2</sub> (g) $H_T^{\circ} - H_{298}^{\circ}$	NbO <sub>2</sub> (solid) $H_T^{\circ} - H_{298}^{\circ}$	Nb $H_T^{\circ} - H_{298}^{\circ}$	O <sub>2</sub> $H_T^{\circ} - H_{298}^{\circ}$
1700	17.149	20.717	27.430	9.279	11.465
1800	18.562	22.271	29.415	10.13	12.354
1900	19.998	23.821	31.400	10.757	13.248
2000	21.459	25.369	33.385	11.510	14.148

In more recent work, Shchukarev et al<sup>10</sup> studied Knudsen effusion from NbO<sub>2</sub>(solid) in a cell of forged molybdenum. Their data were obtained at 1938 to 2122 °K. They gave an equation of the form:

$$\log P(\text{mmHg}) = \frac{-30,300}{T} + 12.4$$

Thus, the heat of sublimation at the average temperature of the experiments is  $138 \pm 2$  kcal/mole.

They gave a standard heat of sublimation  $\Delta H_0^{\circ} = 141 \pm 0.4$  kcal/mole. Their second-law value of  $138 \pm 2$  kcal/mole can now be reduced to data at 298.15°K.



We consider the average temperature to be 2000 °K and the standard heat of formation of  $\text{NbO}_2(\text{g})$  at 298.15 °K becomes

$$\begin{aligned}\Delta H_{f,298.15}^\circ &= \Delta H_{\text{sub}}^\circ, 2000^\circ\text{K} + (H_T^\circ - H_{298}^\circ)\text{NbO}_{2(\text{solid})} \\ &\quad - (H_T^\circ - H_{298}^\circ)\text{NbO}_{2(\text{g})} + \Delta H_f^\circ\text{NbO}_2(\text{s}); 298.15^\circ\text{K} \\ &= 138 + 33.385 - 25.369 - 190.2 \\ &= -44.184 \text{ kcal/mole.}\end{aligned}$$

The vapor pressures of Shchukarev et al<sup>10</sup> can also be analyzed by the third-law method. Free-energy functions for  $\text{NbO}_2(\text{solid})$  and  $\text{NbO}_2(\text{gas})$  were from the present compilation. The results are shown in table 49.

TABLE 49  
THIRD-LAW ANALYSIS OF VAPORIZATION OF  $\text{NbO}_2$  VIA  
THE REACTION  $\text{NbO}_2(\text{solid}) \rightarrow \text{NbO}_2(\text{gas})$

T	P <sub>NbO<sub>2</sub></sub>	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) \text{NbO}_{2(\text{solid})} - \left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) \text{NbO}_{2(\text{gas})}$		$\Delta H_{298.15}^\circ$
(°K)	(atm)	(cal deg K <sup>-1</sup> gfw <sup>-1</sup> )		(kcal gfw <sup>-1</sup> )
1938	7.921 x 10 <sup>-7</sup>	31.111	75.104	139.365
1948	1.0881 x 10 <sup>-6</sup>	31.196	75.169	138.815
1978	1.605 x 10 <sup>-6</sup>	31.450	75.362	139.304
1978	1.539 x 10 <sup>-6</sup>	31.450	75.362	139.469
1992	1.986 x 10 <sup>-6</sup>	31.568	75.452	139.391
2005	2.842 x 10 <sup>-6</sup>	31.676	75.534	138.820
2031	4.197 x 10 <sup>-6</sup>	31.892	75.698	138.942
2037	4.236 x 10 <sup>-6</sup>	31.941	75.736	139.291
2081	9.934 x 10 <sup>-6</sup>	32.300	76.008	138.596
2122	1.473 x 10 <sup>-5</sup>	32.628	76.258	139.499
Average $\Delta H_{298.15}^\circ$				= 139.149

Therefore, the heat of formation of  $\text{NbO}_2(\text{g})$  can be calculated as

$$\begin{aligned}\Delta H_{f298.15; \text{NbO}_2(\text{g})}^\circ &= \Delta H_{f298.15; \text{NbO}_2(\text{solid})}^\circ + \Delta H_{298.15; \text{sublimation}}^\circ \\ &= -190.2 \quad + 139.149\end{aligned}$$

$$\Delta H_{f298.15; \text{NbO}_2(\text{g})}^\circ = -51.051 \text{ kcal gfw}^{-1}.$$

Finally, the heat of formation at  $0^\circ\text{K}$  becomes, for this third-law calculation:

$$\begin{aligned}\Delta H_{f0}^\circ &= \Delta H_{f298.15}^\circ + (H_{298}^\circ - H_0^\circ)_{\text{Nb}} + (H_{298}^\circ - H_0^\circ)_{\text{O}_2} - (H_{298}^\circ - H_0^\circ)_{\text{NbO}_2(\text{g})} \\ &= -51.051 \quad + 1.264 \quad + 2.075 \quad - 2.691\end{aligned}$$

$$\Delta H_{f0}^\circ = -50.403 \text{ kcal gfw}^{-1}.$$

Also, the heat of formation of  $\text{NbO}_2(\text{g})$  at  $0^\circ\text{K}$  is given for the second-law data of Shchukarev et al<sup>10</sup> as:

$$\begin{aligned}\Delta H_{f0^\circ\text{K}}^\circ &= \Delta H_{f298.15}^\circ + (H_{298}^\circ - H_0^\circ)_{\text{Nb}} + (H_{298}^\circ - H_0^\circ)_{\text{O}_2} - (H_{298}^\circ - H_0^\circ)_{\text{NbO}_2} \\ &= -44.184 \quad + 1.264 \quad + 2.075 \quad - 2.691\end{aligned}$$

$$\Delta H_{f0^\circ\text{K}}^\circ = -43.536 \text{ kcal/mole.}$$

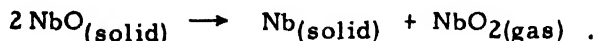
The heat of dissociation of  $\text{NbO}_2(\text{g})$  at  $0^\circ\text{K}$  can also be obtained as:

$$\begin{aligned}\Delta H_{\text{diss}}^\circ &= +43.536 + 171.103 + 2(58.986) \\ &= 332.611 \text{ kcal/mole} = 14.422 \text{ ev.}\end{aligned}$$

A similar calculation for the third-law heat of formation at  $0^\circ\text{K}$  of  $-50.403 \text{ kcal gfw}^{-1}$  leads to a heat of dissociation of  $14.719 \text{ ev.}$

The obtained values for the dissociation energy are somewhat lower than the value of  $14.9 \pm 0.1 \text{ ev}$  calculated by Shchukarev et al.<sup>10</sup> It is not clear wherein the discrepancy lies, although they may have used different auxiliary data. However, it can be noted that Brewer and Rosenblatt<sup>2</sup> had estimated the dissociation energy to be  $320 \pm 25 \text{ kcal/mole}$  which is in agreement with our calculations.

Work on the vaporization of  $\text{NbO}_2(\text{g})$  from  $\text{NbO}(\text{s})$  has been given by Shchukarev et al.<sup>11</sup> They assumed the following reaction:



For this assumed reaction, they found a heat of reaction near 1800 °K of  $140 \pm 3 \text{ kcal gfw}^{-1}$ .

The heat of formation of  $\text{NbO}_2(\text{g})$  at 298.15 °K is then given as:

$$\begin{aligned} \Delta H_f^\circ; \text{NbO}_2(\text{g}); 298.15 &= \Delta H_{\text{reac}}^\circ; 1800^\circ\text{K} + 2(H_T^\circ - H_{298}^\circ)\text{NbO}(\text{s}) - (H_T^\circ - H_{298}^\circ)\text{Nb} \\ &\quad - (H_T^\circ - H_{298}^\circ)\text{NbO}_2(\text{g}) + 2\Delta H_f^\circ\text{NbO}(\text{s}); 298.15 \end{aligned}$$

$$\begin{aligned} \Delta H_f^\circ; \text{NbO}_2(\text{g}); 29.815 &= 140. + 2(18.562) - 10.013 - 22.271 + 2(-97.700) \\ &= -50.560 \text{ kcal/mole.} \end{aligned}$$

Thus, we have available three determinations of the heat of formation of  $\text{NbO}_2(\text{g})$ :

Source	$\Delta H_f^\circ_{298.15} \text{ (kcal/mole)}$
Shchukarev <u>et al</u> <sup>7</sup> (1959)	(from $\text{NbO}_2$ ) -41.487
Shchukarev <u>et al</u> <sup>10</sup> (1962)	(from $\text{NbO}_2$ ) 2 <sup>nd</sup> law -44.184
Shchukarev <u>et al</u> <sup>10</sup> (1962)	(from $\text{NbO}_2$ ) 3 <sup>rd</sup> law -51.051
Shchukarev <u>et al</u> <sup>11</sup> (1962)	(from $\text{NbO}$ ) -50.560

For the present purposes, the 1962 work of Shchukarev et al<sup>10</sup> based on vaporization of  $\text{NbO}_2(\text{g})$  from  $\text{NbO}_2(\text{solid})$  is preferred. The third-law analysis presented here is accepted for the purpose of consistency. Hence, the value of  $\Delta H_f^\circ_{298.15} = -51.051 \text{ kcal/mole}$  is accepted as the heat of formation of  $\text{NbO}_2(\text{g})$ . The uncertainty is believed to be  $\pm 5.000 \text{ kcal/mole}$ .

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#### 16.4.5 Niobium Pentoxide ( $\text{Nb}_2\text{O}_5(s, l)$ )

##### a. Crystal Structure and Melting Points

Brauer<sup>1</sup> made one of the earliest studies of  $\text{Nb}_2\text{O}_5$ . He reported that it can exist as three crystalline modifications, designated L (low), M (middle), and H (high). The amorphous form of  $\text{Nb}_2\text{O}_5$  was converted to the crystalline L form by heating at  $500^\circ\text{C}$ . The M form was obtained at  $1000^\circ\text{C}$  and the H form at  $1100^\circ\text{C}$ . The changes were not reversible, that is the H form could not be converted to the L or M forms by holding at lower temperatures. Brauer reported a melting point of  $1460 \pm 5^\circ\text{C}$ .

Holtzberg et al<sup>2</sup> found that the M and H forms of  $\text{Nb}_2\text{O}_5$  are identical. They reported the following transformation temperatures:

amorphous to  $\gamma$  at  $435^\circ\text{C}$ ;  $\gamma$  to  $\alpha$  at  $830^\circ\text{C}$ , where

$$\gamma \equiv \text{L} \quad \text{and} \quad \alpha = \text{H}$$

Holtzberg et al found a melting point of  $1491^\circ\text{C}$ .

Schafer and Roy<sup>3</sup> found that the low-temperature form of  $\text{Nb}_2\text{O}_5$  converted directly to the high-temperature form at  $800^\circ\text{C}$  by heating under "dry" conditions. These tests did not yield the medium form. In hydrothermal tests, Schafer and Roy found that amorphous  $\text{Nb}_2\text{O}_5$  converted to low-form  $\text{Nb}_2\text{O}_5$  at  $290^\circ\text{C}$  which transformed into the medium form at  $380$  to  $540^\circ\text{C}$ . The medium form then transformed into the high form at  $1060^\circ\text{C}$  which could not be converted back into the other forms by cooling. At temperatures above  $1285^\circ\text{C}$ , a new high temperature form of  $\text{Nb}_2\text{O}_5$  was found. The change at  $1285^\circ\text{C}$  appeared to be reversible and was endothermic. Schafer and Roy found a melting point of  $1465 \pm 5^\circ\text{C}$ .

Schafer and Roy have presented a tentative free energy versus temperature diagram which shows the temperature range of stability for the various  $\text{Nb}_2\text{O}_5$  forms. Their preferred interpretation shows a single phase stable up to  $1060^\circ\text{C}$ ; a high form from  $1060$  to  $1285^\circ\text{C}$ ; and a new high form from  $1285$  to  $1465^\circ\text{C}$ . Liquid  $\text{Nb}_2\text{O}_5$  is considered stable above  $1465^\circ\text{C}$ .

Goldschmidt<sup>4</sup> has considered the medium modification of  $\text{Nb}_2\text{O}_5$  given by Brauer<sup>1</sup> to be the same as the high modifications. Goldschmidt has called the low-temperature form  $\alpha$  corresponding to Brauer's L form, and the high-temperature form  $\beta$ , corresponding to Brauer's H form. On heating, he observes rapid transition at  $900^\circ\text{C}$ , but no transition on cooling. The  $900^\circ\text{C}$  is not unique and is time-dependent. Thus, even at  $600^\circ\text{C}$ . Goldschmidt estimates that  $\alpha$  would be 50 percent transformed into  $\beta$ - $\text{Nb}_2\text{O}_5$ .

At this point, it should be noted that Goldschmidt's nomenclature of using  $\alpha$  for the low-temperature form appears at variance with recent usage. For example, Kofstad<sup>5</sup> and Greener et al<sup>6</sup> have recently made electrical conductivity measurements on  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub> at temperatures from 600 to 1200°C and 900 to 1400°C, respectively. Their usage of  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub> appears to be the same as that of Holtzberg et al.<sup>2</sup>

The  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub> reported by Holtzberg et al<sup>2</sup> was reindexed as a monoclinic unit cell with  $a = 21.34 \text{ \AA}$ ,  $b = 3.816 \text{ \AA}$ ,  $c = 19.47 \text{ \AA}$ , and  $\beta = 120^\circ 20'$ .

From his studies, Goldschmidt<sup>4</sup> concluded that his  $\beta$ -Nb<sub>2</sub>O<sub>5</sub> (the high-temperature form or  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub> of Holtzberg et al<sup>2</sup>) is the stable phase of Nb<sub>2</sub>O<sub>5</sub> up to 1230°C (his experimental range). He also mentions that certain additives can stabilize either the low or high-temperature forms of Nb<sub>2</sub>O<sub>5</sub>.

Reisman and Holtzberg<sup>7</sup> have observed a metastable  $\epsilon$ -Nb<sub>2</sub>O<sub>5</sub> phase which is formed by crystallization from molten Nb<sub>2</sub>O<sub>5</sub> at about 1435°C. This phase transforms irreversibly with evolution of heat to  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub> at 1400 to 1200°C. When  $\epsilon$ -Nb<sub>2</sub>O<sub>5</sub> was heated from 1400°C, it melted at 1435°C. Seeding with  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub> caused freezing and a subsequent melting point of 1495°C which is the value for  $\alpha$ -Nb<sub>2</sub>O<sub>5</sub>. Their results disagree with the proposed diagram of Schafer and Roy<sup>3</sup>.

An X-ray study of the structure of the  $\alpha$ ,  $\beta$ , and  $\gamma$  forms of Nb<sub>2</sub>O<sub>5</sub> has been reported by Zvinchuk.<sup>8</sup>

Diamond and Schneider<sup>9</sup> measured the melting point of Nb<sub>2</sub>O<sub>5</sub> in a solar furnace. They obtain a value of 1496°C in good agreement with data already presented. However, they noted that their method did not give good results in all cases. The homogeneity range for Nb<sub>2</sub>O<sub>5</sub> has been stated to be NbO<sub>2.5</sub> to NbO<sub>2.39</sub> by Brauer<sup>1</sup> and NbO<sub>2.5</sub> to NbO<sub>2.42</sub> by Grube and Flad,<sup>10</sup> and quoted by Kubaschewski and Catterall.<sup>11</sup>

In reviewing the available data for Nb<sub>2</sub>O<sub>5</sub>, it is seen that there are several conflicting types of data. It appears likely that many of the observed polymorphs are metastable. It is possible that there are several stable forms of Nb<sub>2</sub>O<sub>5</sub>, but in view of the irreversibility of the phase transitions reported, it appears likely that most of the observed phases are metastable.

For the present work, we consider the high-temperature phase (H-form of Brauer<sup>1</sup> or  $\alpha$  form of Holtzberg et al<sup>2</sup>) as the stable phase. It is to be noted that this phase was also used by Orr<sup>12</sup> in his heat-content measurements. Orr had preheated his material to convert it to the high-temperature form. His results did not show any phase

transitions other than the melting one at 1785 °K (1512 °C). He had observed premelting over the range of 1750 to 1785 °K (1477 to 1512 °C).

Accordingly, in the following tables we consider the Nb<sub>2</sub>O<sub>5</sub> to be in the so-called  $\alpha$  or high form up to the melting point of 1785 °K.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

Kelley and King<sup>13</sup> list the low-temperature measurements of King<sup>14</sup> as having been performed over the range 51 to 298.15 °K. He performed his experiments on the  $\alpha$ -or high-temperature form of Nb<sub>2</sub>O<sub>5</sub>. His data yielded  $S_{298.15}^\circ = 32.8 \pm 0.2$  eu. for the entropy of Nb<sub>2</sub>O<sub>5</sub>. This value is accepted in the present calculations. No data were tabulated for  $H_{298.15}^\circ - H_0^\circ$ . However, an integration of the data reported by King<sup>14</sup> was done here which gave  $H_{298.15}^\circ - H_0^\circ = 5.325$  kcal/gfw.

### 2) High-temperature heat content

In his tabulation, Kelley<sup>15</sup> lists high-temperature heat capacity measurements by Kruss and Nilson<sup>16</sup> for the range 273 to 713 °K and by Orr<sup>12</sup> for the range of 298 to 1809 °K. Kelley<sup>15</sup> derived an equation of the form  $C_p^\circ = 36.90 + 5.12 \times 10^{-3} T - 6.10 \times 10^{-5} T^2$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> for the range 298.15 to 1785 °K. The heat of fusion was found to be 24,590 cal gfw<sup>-1</sup>. Measurements in the liquid range indicated that the heat capacity was  $C_p^\circ = 57.90$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>. The original equation given by Orr<sup>12</sup> differs somewhat from the Kelley equation, i. e., Orr reported  $C_p^\circ = 36.23 + 5.54 \times 10^{-3} T^2 - 4.88 \times 10^{-5} T^2$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

Gel'd and Kusenko<sup>17</sup> measured the heat capacity of Nb<sub>2</sub>O<sub>5</sub> as well as several other lower oxides. For Nb<sub>2</sub>O<sub>5</sub> they reported no transitions and found

$$C_p^\circ = 38.76 + 3.54 \times 10^{-3} T - 7.318 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

for the range 298.15 to 1740 °K.

In comparing the Kelley equation with that of Gel'd and Kusenko, it is seen that at 1000 °K the Kelley equation gives  $C_p^\circ = 41.41$ , and the Gel'd and Kusenko equation gives  $C_p^\circ = 41.57$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> with a difference of 0.38 percent. In view of the good agreement, and the fact that his data cover a wider range, the data reported by Kelley<sup>15</sup> are utilized.

### 3) Heat of formation

In recent years, the great interest in niobium and its compounds has resulted in considerable data on the heat of formation of  $\text{Nb}_2\text{O}_5$ . Values reported are listed in table 50.

TABLE 50

HEAT-OF-FORMATION VALUES ( $\Delta H_{f298.15}^\circ$ ) REPORTED FOR  $\text{Nb}_2\text{O}_5$

$\Delta H_{f298.15}^\circ$ (kcal/gfw)	Reference	Year
-442.8	Muthmann <u>et al</u> <sup>18</sup>	1907
-463.1 $\pm$ 0.7	Becker and Roth <sup>19</sup>	1933
-455.2 $\pm$ 0.6	Humphrey <sup>20</sup>	1954
-472.6 $\pm$ 1.0	Morozova and Getskina <sup>21</sup>	1959
-454.8 $\pm$ 0.8	Morozova and Stolyarova <sup>22</sup>	1960
-458.6 $\pm$ 5.0	Kusenko and Gel'd <sup>23</sup>	1960
-455.1 $\pm$ 0.5	Kusenko and Gel'd <sup>24</sup>	1960
-454.4 $\pm$ 1.6*	Huber <u>et al</u> <sup>25</sup>	1961
-453.5 $\pm$ 0.4	Kornilov <u>et al</u> <sup>26</sup>	1962
-453.5 $\pm$ 0.4**	Kornilov <u>et al</u> <sup>27</sup>	1962
-456.9	Lavrent'ev <u>et al</u> <sup>28</sup>	1961

\*They recommend use of Humphrey's<sup>20</sup> value of -455.2 kcal gfw<sup>-1</sup>.

\*\*The value is given for the  $\beta$ - $\text{Nb}_2\text{O}_5$  reported by Goldschmidt<sup>4</sup>, i. e., it corresponds to the H form, or high-temperature form or  $\alpha$ - $\text{Nb}_2\text{O}_5$  referred to by Brauer<sup>1</sup> or Holtzberg.<sup>2</sup>

Referring to the data in table 50, the following calorimetric values appear to be most precise:

TABLE 51

MOST ACCURATE HEAT-OF-FORMATION VALUES FOR  $\text{Nb}_2\text{O}_5$

-455.2 $\pm$ 0.6	Humphrey <sup>20</sup>	1954
-454.8 $\pm$ 0.8	Morozova and Stolyarova <sup>22</sup>	1960
-455.1 $\pm$ 0.5	Kusenko and Gel'd <sup>24</sup>	1960
-454.4 $\pm$ 1.6	Huber <u>et al</u> <sup>25</sup>	1961
-453.5 $\pm$ 0.4	Kornilov <u>et al</u> <sup>26, 27</sup>	1962

average  $\Delta H_{f298.15}^\circ = -454.6$  kcal/gfw.



This final, average value is then selected as the heat of formation of  $\text{Nb}_2\text{O}_5$ . In assessing the five calorimetric determinations, the good agreement contrasts with many of the discordant results obtained for other compounds. However, it may be fruitful to make some comparisons as shown in table 52. Based on overall purity, it would appear that Humphrey<sup>20</sup> had the highest purity sample. However, his analyses were spectrographic, which would not show the presence of oxygen, carbon, nitrogen, and hydrogen impurities. Another minor problem with the Humphrey data is that the percentage conversions into  $\text{Nb}_2\text{O}_5$  were somewhat low, necessitating a larger correction factor. Kubaschewski and Catterall<sup>11</sup> (p. 166) have noted that less heat is needed to convert  $\text{Nb}_2\text{O}_5\text{-x}$  into  $\text{Nb}_2\text{O}_5$  than by the linear corrections which Humphrey used. Kubaschewski and Catterall made a correction on such a basis which yielded a value of -454.02 kcal/gfw instead of -455.2 kcal/gfw as reported by Humphrey.

The work by Kornilov et al<sup>26, 27</sup> appears to have been well done. Their percentage conversions were quite high, although their sample purities were somewhat less than those of other investigators.

Huber et al<sup>25</sup> utilized a powdered sample and they felt that the Humphrey determination should be favored.

The details of the investigations by Kusenkov and Gel'd<sup>24</sup> and Morozova and Stolyarova<sup>22</sup> are not as clear as for the other works, and may not have been as comprehensive.

In general, there seems to be some indication that a lower heat of formation as found recently by Kornilov et al<sup>26, 27</sup> should be favored. However, at the present time, it is felt that an average of five separate determinations should be preferred to a single determination. Accordingly, the average value of  $\Delta H_{f298.15}^\circ = -454.6$  kcal/gfw is accepted.

In addition to the calorimetric data already referred to there have been other equilibria measurements performed involving  $\text{Nb}_2\text{O}_5$ . The work of Lavrent'ev et al<sup>28</sup> already referred to utilized hydrogen reduction of  $\text{Nb}_2\text{O}_5$  to  $\text{NbO}_2$  and  $\text{NbO}_2$  to  $\text{NbO}$  in the temperature range 1200° to 1550°C. They used emf measurements to

TABLE 52

COMPARISON OF CALORIMETRY DATA FOR  $Nb_2O_5$ 

	Humphrey <sup>20</sup>	Kornilov et al. <sup>26, 27</sup>		Huber et al. <sup>25</sup>	Kusenko and Gelfond <sup>24</sup>	Morozova and Stolyarova <sup>22</sup>
Type of niobium	sheet	bulk		powdered	----	bulk
Pressure of $O_2$ , atm	30	30		25	----	33, 88 <sup>a</sup>
Temperature ( $^{\circ}C$ ) of calorimeter	30	25, 3		25, 2	----	18 <sup>a</sup>
Percentage completion	97, 63-99, 38	99, 48-99, 90		98, 78-100	99, 1-99, 33	----
Chemical analysis						
(wt %) Nb	0, difference) 99, 99	No. 1 99, 35	No. 2 99, 47	99, 45	99, 01	99, 49
La	0, 20	0, 30	1, 27	0, 00	0, 94	0, 51
O	----	0, 03	0, 015	0, 130	0, 04	
N	---	0, 03	0, 01	0, 094		
H	----	0, 004	----	0, 004		
C	----	0, 02	0, 005	0, 018		0, 01
Fe	<0, 01	0, 09	0, 07	0, 065		
Pb	----	0, 12	0, 12			
Si	<0, 01	0, 06	0, 04			
W	0, 05	----	----			
Mo	<0, 01	----	----			
B	<0, 01	----	----			
Al	<0, 005	---	----			
Mn	<0, 005	----	----			
Ni	<0, 005	---	----			
Zr	<0, 005	----	----			

<sup>a</sup>Morozova and Stolyarova<sup>22</sup> do not give these figures, but the earlier investigation by Morozova and Getskina<sup>21</sup> lists a pressure of 35 kg/cm<sup>2</sup> and 15 $^{\circ}C$ .

obtain data for NbO, since H<sub>2</sub> could not reduce oxides below the NbO stage. Lyubimov and Gel'd<sup>29</sup> have also studied the hydrogen reduction of niobium oxides and obtained equilibria constants,  $K_p = P(H_2O)/P(H_2)$  which differed from earlier reported data. Brewer<sup>30</sup> has reviewed older hydrogen reduction data of Grube, Kubaschewski, and Zwiauer,<sup>31</sup> Sue,<sup>32</sup> and Schaefer and Breil.<sup>33</sup>

Equilibria in the Nb-C-O system have also been studied by several investigators. Kusenko and Gel'd<sup>34</sup> have studied this system and have referred to other work as well. Some of this work has been performed by Shveikin,<sup>35</sup> Kolchin et al.,<sup>36</sup> Sazhin et al.,<sup>37</sup> and Shveikin et al.<sup>38</sup>

Vaporization studies of niobium oxides have been made with a mass spectrometer by Shchukarev et al.<sup>39, 40, 41</sup>

Further studies of the affinity of oxygen for niobium have been reported by Meerson and Segorceanu.<sup>42</sup>

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## 17. Nitrogen Compounds

In this report, boron, carbon, nitrogen, and oxygen are normally considered to be nonmetallic elements, and therefore, such compounds as are formed by combining one of these nonmetallic elements with one of the 31 metallic elements are discussed under the appropriate metallic constituent in section IVB. Borides, carbides, nitrides, and oxides which could be found in the present category are discussed below.

### 17.1 Nitrogen Borides

The borides of nitrogen (more commonly called boron nitrides) are referred to in section 2.3.

### 17.2 Nitrogen Carbides

The carbides of nitrogen (also called carbon nitrides) were not investigated.

### 17.3 Nitrogen Nitrides

Semantically, the term "nitrogen nitrides" has no correct meaning; however for the purposes of this report, this term is considered to denote elemental nitrogen (section IVA17).

### 17.4 Nitrogen Oxides

The oxides of nitrogen were not investigated.

## 18. Osmium Compounds

The only osmium compounds investigated in this study were the oxides.

### 18.1 Osmium Borides

The borides of osmium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 18.2 Osmium Carbides

The carbides of osmium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 18.3 Osmium Nitrides

The nitrides of osmium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 18.4 Osmium Oxides

In this study, detailed analyses of osmium oxides were made for  $\text{OsO}_2(\text{g})$ ,  $\text{OsO}_3(\text{g})$ , and  $\text{OsO}_4(\text{g})$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).



#### 18.4.1 Osmium Monoxide (OsO(g))

No spectroscopic data were available for gaseous osmium monoxide. A vibration frequency of  $795\text{ cm}^{-1}$  and an internuclear distance of  $1.84\text{Å}$  were estimated for this molecule. No attempt was made to include estimates of the contributions of electronic levels above the ground state. The latter was assigned a multiplicity of 6. Based on the above estimates, the following spectroscopic constants were derived and used in the calculation of the thermodynamic functions of gaseous osmium monoxide (units of  $\text{cm}^{-1}$  except for g):

$g$	$\omega_e$	$\omega_e x_e$	$B_e$	$a_e$	$D_e$
6	795	3.6	0.34	0.0019	$2.4 \times 10^{-7}$

Brewer and Chandrasekharaiah<sup>1</sup> estimated the vibration frequency and internuclear distance to be  $785\text{ cm}^{-1}$  and  $1.85\text{Å}$ , respectively.

The value of  $D_0^\circ$  for OsO(g) was estimated to be  $(1/3)D_0^\circ(\text{OsO}_3(\text{g}))$  from section IVB18.4.3, and the following quantities were calculated:

$$D_{298}^\circ(\text{OsO}(\text{g})) = 145\text{ kcal/gfw.} \quad (\text{IVB18.4.1-1})$$

$$\Delta H_{f298}^\circ(\text{OsO}(\text{g})) = 102 \pm 20\text{ kcal/gfw} \quad (\text{IVB18.4.1-2})$$

#### REFERENCE FOR SECTION IVB18.4.1

1. Brewer, L. and M.S. Chandrasekharaiah, U.S. At. Energy Comm. Rept. UCRL-8713, Rev. (June 1960).

#### 18.4.2 Osmium Dioxide (OsO<sub>2</sub>(g))

No experimental spectroscopic data had been reported for gaseous OsO<sub>2</sub>. All of the molecular constants required for the calculation of the thermodynamic functions of OsO<sub>2</sub> were, therefore, estimated. The thermodynamic functions for gaseous OsO<sub>2</sub> were calculated with the following molecular data:

Molecular configuration:

Symmetric, linear molecule

$$r_{\text{Os-O}} = 1.85\text{Å}.$$

Moment of inertia:

$$I = 181.831 \times 10^{-40}\text{ g cm}^2$$

$$B = 0.1539\text{ cm}^{-1}.$$

Symmetry number:

$$\theta = 2.$$

Fundamental frequencies:

$$\omega_1 = 764 \text{ cm}^{-1}$$

$$\omega_2 = 215 \text{ cm}^{-1} \text{ (multiplicity} = 2)$$

$$\omega_3 = 825 \text{ cm}^{-1}.$$

Ground electronic state:

$$^1\Sigma.$$

The molecular configuration of  $\text{OsO}_2$  was unknown. Consideration of the periodic group to which osmium belongs led to the assumption that  $\text{OsO}_2$  is a symmetric, linear molecule. The Os-O bond distance in  $\text{OsO}_2$  was assumed to be the same as that estimated for the corresponding osmium monoxide ( $\text{OsO}$ ) molecule.<sup>1</sup>

The moment of inertia of  $\text{OsO}_2$  was calculated by means of equation (IVB18.4.2-1).

$$I = 2M_{\text{O}}r^2, \quad (\text{IVB18.4.2-1})$$

where  $M_{\text{O}}$  is the mass of oxygen atom, and  $r$  is the Os-O bond distance.

The fundamental frequencies of  $\text{OsO}_2$  were estimated by the method described in section IIIB1 of this report.

The electronic states of  $\text{OsO}_2$  were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a  $^1\Sigma$  state was followed.

For the estimation of the value of  $\Delta H_{f298}^\circ$  for  $\text{OsO}_2(g)$ , it was assumed that  $D_0^\circ(\text{OsO}_2(g))$  is  $(2/3) D_0^\circ(\text{OsO}_3(g))$ . The following quantities were then calculated:

$$D_{298}^\circ(\text{OsO}_2(g)) = 289 \text{ kcal/gfw}, \quad (\text{IVB18.4.2-2})$$

$$\Delta H_{f298}^\circ(\text{OsO}_2(g)) = 17.4 \pm 10 \text{ kcal/gfw}. \quad (\text{IVB18.4.2-3})$$

Brewer and Rosenblatt<sup>2</sup> estimated  $D_{298}^\circ$  for  $\text{OsO}_2(g)$  to be  $255 \pm 15 \text{ kcal/gfw}$ .

## REFERENCES FOR SECTION IVB18. 4. 2

1. Brewer, L. and M. S. Chandrasekharaiah, U.S. At. Energy Comm. Rept. UCRL-8713, Rev. (June 1960).
2. Brewer, L. and G. M. Rosenblatt, Chem. Revs. 61, 257 (1961).

### 18. 4. 3 Osmium Trioxide (OsO<sub>3</sub>(g))

Experimental spectroscopic data had not been reported for gaseous OsO<sub>3</sub>. The thermodynamic functions in the ideal gas table for OsO<sub>3</sub> were calculated with the following estimated molecular data:

Molecular configuration:

Planar, symmetric, cart-wheel molecule

$$r_{\text{Os-O}} = 1.85 \text{ \AA}.$$

Product of moments of inertia:

$$I_A I_B I_C = 5.072420 \times 10^{-114} \text{ g}^3 \text{ cm}^6.$$

Symmetry number:

$$\theta = 6.$$

Fundamental frequencies:

$$\omega_1 = 764 \text{ cm}^{-1}$$

$$\omega_2 = 291 \text{ cm}^{-1}$$

$$\omega_3 = 811 \text{ cm}^{-1} \text{ (multiplicity} = 2\text{)}$$

$$\omega_4 = 292 \text{ cm}^{-1} \text{ (multiplicity} = 2\text{)}.$$

Ground electronic state:

$$^1\Sigma.$$

The molecular configuration of OsO<sub>3</sub> was unknown. The molecule was assumed to be of the symmetric, planar, cart-wheel type. The Os-O bond distance was assumed to be identical with the estimated distance for the osmium monoxide molecule.<sup>1</sup>

The moments of inertia of  $\text{OsO}_3$  were calculated for the assumed structure by means of equations (IVB18.4.3-1), (IVB18.4.3-2), and (IVB18.4.3-3).

$$I_x = I_y = \left(\frac{3}{2}\right) M_O r^2 \quad , \quad (\text{IVB18.4.3-1})$$

$$I_z = I_x + I_y \quad , \quad (\text{IVB18.4.3-2})$$

$$I_A I_B I_C = I_x I_y I_z \quad , \quad (\text{IVB18.4.3-3})$$

where  $M_O$  is the mass of oxygen atom, and  $r$  is the Os-O bond distance.

The fundamental frequencies of  $\text{OsO}_3$  were estimated by the method described in section IIIB3 of this report.

The electronic states of  $\text{OsO}_3$  were unknown. The general practice, when no data are available, of considering only the ground state and assuming it to be a  $^1\Sigma$  state was followed.

Grimley, Burns, and Inghram<sup>2</sup> made a mass spectrometric study of the vaporization of osmium metal in oxygen atmospheres and calculated a heat of reaction of  $11.8 \pm 1$  kcal/gfw at 1400°K for reaction (IVB18.4.3-4).



With the heat contents of  $\text{OsO}_4(\text{g})$ ,  $\text{OsO}_3(\text{g})$ , and  $\text{O}_2$  from the present compilation, the heat of the reaction at 298.15°K was calculated to be 12.7 kcal/gfw. The value of  $M_{f298}^\circ$  for  $\text{OsO}_3(\text{g})$  of  $-67.8 \pm 8.0$  kcal/gfw was, therefore, adopted herein. The heats of dissociation to the gaseous atoms were calculated to be

$$D_{298}^\circ(\text{OsO}_3(\text{g})) = 133.9 \text{ kcal/gfw} \quad (\text{IVB18.4.3-5})$$

$$D_0^\circ(\text{OsO}_3(\text{g})) = 430.9 \text{ kcal/gfw} \quad (\text{IVB18.4.3-6})$$

From the data of Grimley, Burns, and Inghram<sup>2</sup> and data for  $\text{OsO}_4(\text{g})$ , Alcock<sup>3</sup> derived an expression for the free energy of formation of  $\text{OsO}_3(\text{g})$  from which  $D_0^\circ$  can be calculated to be 432 kcal/gfw, and  $M_{f298}^\circ$  can be calculated to be -60.2 kcal/gfw, when the entropies for  $\text{OsO}_3(\text{g})$  and  $\text{OsO}_4(\text{g})$  from the present compilation are used.

## REFERENCES FOR SECTION IVB18.4.3

1. Brewer, L. and M. S. Chandrasekhariah, U. S. At. Energy Comm. Rept. UCRL-8713, Rev. (June 1960).
2. Grimley, R. T., R. P. Burns, and M. G. Inghram, J. Chem. Phys. 33, 308 (1960).
3. Alcock, C. B., Platinum Metals Rev. 5, 134 (1961).

### 18.4.4 Osmium Tetroxide ( $\text{OsO}_4(g)$ )

The thermodynamic functions for gaseous  $\text{OsO}_4$  were calculated with the following molecular data:

Molecular configuration:

Regular tetrahedron

$$r_{\text{Os-O}} = 1.85 \text{ \AA}.$$

Product of moments of inertia:

$$I_A I_B I_C = 1.4250638 \times 10^{-113} \text{ g}^3 \text{ cm}^6.$$

Symmetry number:

$$\theta = 12.$$

Fundamental frequencies:

$$\omega_1 = 971 \text{ cm}^{-1}$$

$$\omega_2 = 328 \text{ cm}^{-1} \text{ (multiplicity} = 2\text{)}$$

$$\omega_3 = 959.7 \text{ cm}^{-1} \text{ (multiplicity} = 3\text{)}$$

$$\omega_4 = 328 \text{ cm}^{-1} \text{ (multiplicity} = 3\text{)}.$$

Ground electronic state:

$$^1\Sigma.$$

The regular tetrahedral configuration of  $\text{OsO}_4$  had been established by infrared and Raman spectral data.<sup>1-4</sup> The Os-O bond distance was still open to question.<sup>3-8</sup> The value given by Dodd;<sup>3</sup> i. e., 1.85 Å, was accepted in the present work.

The moments of inertia for the  $\text{OsO}_4$  molecule was calculated by means of equations (IVB18. 4. 4-1) and (IVB18. 4. 4-2).

$$I_x = I_y = I_z = \left(\frac{8}{3}\right) M_O r^2 \quad , \quad (\text{IVB18. 4. 4-1})$$

$$I_A I_B I_C = I_x I_y I_z \quad , \quad (\text{IVB18. 4. 4-2})$$

where  $M_O$  is the mass of oxygen atom, and  $r$  is the Os-O bond distance.

The values of  $\omega_2$ ,  $\omega_3$ , and  $\omega_4$  are those observed by Hawkins and Sabol<sup>4</sup> in an infrared study of gaseous  $\text{OsO}_4$ , while  $\omega_1$  is that reported by Langseth and Qvillar<sup>2</sup> from a Raman study of the gas. These values differ only slightly from the values reported by Woodward and Roberts<sup>1</sup> for liquid  $\text{OsO}_4$ .

The electronic states of  $\text{OsO}_4$  were not known. A  $^1\Sigma$  ground state was assumed.

The heat of formation of  $\text{OsO}_4(\text{g})$  at 298.15°K given by Coughlin,<sup>9</sup> -80,500 ± 6.5 Kcal/gfw, was adopted herein. This quantity had been derived from the heat of formation of the yellow form of solid  $\text{OsO}_4$  as determined by von Wartenberg<sup>10</sup> and the heat of sublimation of this solid as given by Kelley.<sup>11</sup> From this heat of formation and the values of  $H_{298}^\circ - H_0^\circ$  for the appropriate molecules and the heat of sublimation of osmium from this compilation, the heats of dissociation of  $\text{OsO}_4(\text{g})$  to gaseous atoms at 298.15° and 0°K were calculated to be

$$D_{298}^\circ(\text{OsO}_4(\text{g})) = 506.1 \text{ kcal/gfw} \quad . \quad (\text{IVB18. 4. 4-3})$$

$$D_0^\circ(\text{OsO}_4(\text{g})) = 501.9 \text{ kcal/gfw} \quad . \quad (\text{IVB18. 4. 4-4})$$

#### REFERENCES FOR SECTION IVB18. 4. 4

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2. Langseth, A. and B. Qvillar, Z. Physik, Chem. B27, 90 (1934).
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4. Hawkins, M. J. and W. W. Sabol, *J. Chem. Phys.* 25, 775 (1956).
5. Ortner, M. H., *J. Chem. Phys.* 34, 556 (1961).
6. Woodward, L. A., J. A. Creighton, and K. K. Taylor, *Trans. Faraday Soc.* 56, 1267 (1960).
7. Brockway, *Rev. Mod. Phys.* 8, 260 (1936).
8. Braune, H. and K. W. Stute, *Angew. Chem.* 51, 528 (1938).
9. Coughlin, J. P., *Bur. Mines, Bull.* 542 (1954).
10. von Wartenberg, H., *Ann. Chem.* 440, 97 (1924).
11. Kelley, K. K., *Bur. Mines, Bull.* 383 (1935).

## 19. Oxygen Compounds

In this report, boron, carbon, nitrogen, and oxygen are normally considered to be nonmetallic elements, and therefore, such compounds as are formed by combining one of these nonmetallic elements with one of the 31 metallic elements are discussed under the appropriate metallic constituent in section IVB. Borides, carbides, nitrides, and oxides which could be found in the present category are discussed below.

### 19.1 Oxygen Borides

The borides of oxygen (more commonly called boron oxides) are referred to in section 2.4.

### 19.2 Oxygen Carbides

The carbides of oxygen (more commonly called carbon oxides) were not investigated.

### 19.3 Oxygen Nitrides

The nitrides of oxygen (more commonly called nitrogen oxides) were not investigated.

### 19.4 Oxygen Oxides

Semantically, the term "oxygen oxides" has no correct meaning; however for the purpose of this report, this term is considered to denote elemental oxygen (section IVA 19).



## 20. Platinum Compounds

The only platinum compounds investigated in this study were the oxides.

### 20.1 Platinum Borides

The borides of platinum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 20.2 Platinum Carbides

The carbides of platinum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 20.3 Platinum Nitrides

The nitrides of platinum were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 20.4 Platinum Oxides

In this study, detailed analyses of platinum oxides were made for  $\text{PtO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 20.4.1 Platinum Monoxide ( $\text{PtO}_{(g)}$ )

No spectroscopic data were available for  $\text{PtO}_{(g)}$ . The calculation of the thermodynamic functions was made with the assumption that the molecule was a harmonic oscillator. The vibration frequency was estimated to be  $785\text{ cm}^{-1}$ . From an estimated internuclear distance of  $1.85\text{ \AA}$ , a value for  $B_e$  of  $0.334\text{ cm}^{-1}$  was calculated. A multiplicity of 6 was assumed for the single electronic state used in the calculation.

The dissociation energy of  $\text{PtO}_{(g)}$  at  $0^\circ\text{K}$  was taken to be one-half that for  $\text{PtO}_2^{1,2}$  or  $105\text{ kcal/gfw}$ . The value of  $\Delta H_{f298}^\circ$  calculated from this value of  $D_{0_0}^\circ$  was  $88.6\text{ kcal/gfw}$ . An uncertainty of  $\pm 15\text{ kcal/gfw}$  was assigned to  $\Delta H_{f298}^\circ$ .

#### REFERENCES FOR SECTION IVB20.4.1

1. Brewer, L. and M. Rosenblatt, Chem.Revs. 61, 257 (1961).
2. Alcock, C. B., Plat. Met. Rev. 5, 134 (1961).

## 21. Rhenium Compounds

The only rhenium compounds investigated in this study were the oxides.

### 21.1 Rhenium Borides

The borides of rhenium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 21.2 Rhenium Carbides

The carbides of rhenium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 21.3 Rhenium Nitrides

The nitrides of rhenium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 21.4 Rhenium Oxides

In this study, detailed analyses of rhenium oxides were made for  $\text{ReO}_{(g)}$  and  $\text{Re}_2\text{O}_7(s, l)$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 21.4.1 Rhenium Monoxide ( $\text{ReO}_{(g)}$ )

No spectroscopic data were available for gaseous  $\text{ReO}$ . The following values of  $\omega_e$  and  $r_e$  were estimated for this molecule:

$\omega_e$	$r_e$	$B_e$
$\text{cm}^{-1}$	$\text{\AA}$	$\text{cm}^{-1}$
858 (760)	1.80 (1.82)	0.355

Values in parentheses were estimated by Brewer and Chandrasekharaiah.<sup>1</sup>  $B_e$  was calculated from the estimated  $r_e$  by the relation

$$B_e = \frac{1.686 \times 10^{-15}}{\mu r_e^2} \quad (\text{IVB21.4.1-1})$$

where  $B_e$  is in units of  $\text{cm}^{-1}$ ,  $\mu$  is the reduced mass in mass units, and  $r_e$ , the equilibrium internuclear distance, is in cm.

Thermodynamic functions for gaseous ReO were calculated with the above constants (equivalent to assuming that the molecule is a rigid rotator and harmonic oscillator) from the assumption of the existence of only a ground electronic state with a statistical weight of 1.

$D_0^\circ$  for ReO(g) was estimated to be 154 kcal/gfw from a comparison of adopted dissociation energies of monoxides of elements neighboring rhenium in the periodic table. A  $\Delta H_{f298}^\circ$  for ReO(g) of 90.000 kcal/gfw was then calculated with appropriate thermodynamic functions from the present compilation. An uncertainty of  $\pm 15.000$  kcal/gfw was assigned to  $\Delta H_{f298}^\circ$ .

#### REFERENCE FOR SECTION IVB21.4.1

1. Brewer, L. and M. S. Chandrasekharaiah, U. S. At. Energy Comm. Rept. UCRL-8713 (Rev.) (1960).

#### 21.4.2 Rhenium Heptoxide ( $\text{Re}_2\text{O}_7(s,l)$ )

##### a. Crystal Structure

Preliminary investigations of the crystal structure of  $\text{Re}_2\text{O}_7$  by Wilhelmi<sup>1</sup> indicate an orthorhombic unit cell with cell parameters:

$$a = 15.25 \pm 0.1 \text{ \AA}, b = 5.48 \pm 0.02 \text{ \AA}, c = 12.5 \pm 0.1 \text{ \AA}.$$

A density of  $6.103 \text{ g/cm}^3$  has been measured by Biltz and Lehrer.<sup>2</sup>

##### b. Thermodynamic Properties of Condensed Phases

###### 1) Entropy and heat content at 298.15°K

From the low-temperature heat-capacity measurements of Busey,<sup>3</sup>  $S_{298}^\circ$  and  $H_{298}^\circ - H_0^\circ$  have been calculated to be  $49.543 \pm 0.050$  e. u. and  $7246 \pm 8$  cal/gfw, respectively. From the data of Busey, the heat capacity at 298.15°K is taken as  $39.73 \pm 0.04 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

## 2) Melting point and heat of fusion

A melting point of 574°K has been obtained by Biltz and Lehrer<sup>2</sup> in an early determination. The vapor pressures of solid and liquid  $\text{Re}_2\text{O}_7$  have been determined by Ogawa,<sup>4</sup> and by Smith, Line, and Bell.<sup>5</sup> The data of Ogawa, as well as vapor-density measurements by Noddack and Noddack,<sup>6</sup> indicate  $\text{Re}_2\text{O}_7$  vaporizes without decomposition. From the simultaneous solution of the vapor-pressure equations for the solid and the liquid, Ogawa has calculated a melting point of 569°K. The observed melting point is 570°K. Smith *et al*<sup>5</sup> have obtained a melting point of 573°K from the simultaneous solution of the vapor-pressure equations for the solid and liquid  $\text{Re}_2\text{O}_7$ . This value agrees with their direct determination of the melting point in a sealed tube. The vapor-pressure data of Smith *et al* are in very good agreement with Ogawa's.<sup>4</sup> From these two sets of data, average vapor-pressure curves have been obtained for the solid and liquid  $\text{Re}_2\text{O}_7$ . A melting point of 570°K has been calculated from the intersection of the solid and liquid vapor-pressure curves. The heat of sublimation of the solid and the heat of vaporization of the liquid at the melting point have been obtained from the average vapor-pressure curves. The calculated heat of fusion is  $15.0 \pm 0.5$  kcal/gfw.

## 3) High-temperature heat content

The heat capacity of the solid has been extrapolated from 298° to 570°K by use of the equation:

$$C_p^\circ(s) = 29.15 + 4.4 \times 10^{-2} T - \frac{2.25 \times 10^5}{T^2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Derivation of this equation has been accomplished by reference to the low-temperature data in the region of 250° to 312°K. These data by Busey<sup>3</sup> have already been cited. The heat capacity of the liquid is estimated to be  $71.10 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  over the short liquid range.

## 4) Boiling point and heat of vaporization

From the average vapor-pressure curve obtained for the liquid, a normal boiling point of 634°K has been calculated. The calculated heat of vaporization at this boiling temperature obtained from this curve is  $17.3 \pm 0.5$  kcal/gfw.

5) Standard heat of formation at 298.15 °K

Roth and Becker<sup>7</sup> have determined the heat of formation of  $\text{Re}_2\text{O}_7$  by combustion calorimetry. Their data have been recalculated and summarized in the U.S. National Bureau of Standards' Selected Values of Chemical Thermodynamic Properties (1948). The standard heat of formation reported is  $-297.5 \pm 2.0$  kcal/gfw. More recently, Boyd, Cobble, and Smith<sup>8</sup> have re-determined the heat by combustion calorimetry and obtained  $-295.9 \pm 2.0$  kcal/gfw. The average of  $-296.7 \pm 2.0$  kcal/gfw is adopted here.

c. Thermodynamic Properties of Gaseous Phases

No experimental spectroscopic data have been reported for gaseous rhenium heptoxide. The structure of the  $\text{Re}_2\text{O}_7$  molecule is unknown. Since several possible structures could be written for this molecule, each with different molecular constants, calculation of thermodynamic properties from estimated molecular constants has not been attempted.

REFERENCES FOR SECTION IVB21.4.2

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## 22. Rhodium Compounds

The only rhodium compounds investigated in this study were the oxides.

### 22. 1 Rhodium Borides

The borides of rhodium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 22. 2 Rhodium Carbides

The carbides of rhodium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 22. 3 Rhodium Nitrides

The nitrides of rhodium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 22. 4 Rhodium Oxides

In this study, detailed analyses of rhodium oxides were made for  $\text{RhO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 22. 4. 1 Rhodium Monoxide ( $\text{RhO}_{(g)}$ )

In the absence of spectroscopic data, the  $\text{RhO}_{(g)}$  molecule was assumed to be a rigid rotator and harmonic oscillator. The vibration frequency was estimated to be  $820 \text{ cm}^{-1}$ .  $B_e$  was taken to be  $0.373 \text{ cm}^{-1}$  from an estimated internuclear distance of  $1.81 \text{ \AA}$ . A multiplicity of 4 was assumed for the single electronic state used in the calculation.

The dissociation energy of  $\text{RhO}_{(g)}$  at  $0^\circ \text{K}$  was assumed to be one-half that of the corresponding quantity for  $\text{RhO}_2(g)$ ,<sup>1,2</sup> or  $103 \text{ kcal/gfw}$ . From the assumed  $D_0$ ,  $\Delta H_{f298}^\circ$  was calculated to be  $88.4 \text{ kcal/gfw}$ . An uncertainty of  $\pm 15 \text{ kcal/gfw}$  was assigned to  $\Delta H_{f298}^\circ$ .

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## 23. Samarium Compounds

Detailed analyses were not made for these compounds.

### 23.1 Samarium Borides

The borides of samarium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 23.2 Samarium Carbides

The carbides of samarium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 23.3 Samarium Nitrides

The nitrides of samarium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 23.4 Samarium Oxides

The oxides of samarium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

## 24. Scandium Compounds

Detailed analyses were not made for these compounds; however, elemental scandium is discussed in section IVA 24 of this study.

### 24.1 Scandium Borides

The borides of scandium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 24.2 Scandium Carbides

The carbides of scandium were investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 24.3 Scandium Nitrides

The nitrides of scandium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 24.4 Scandium Oxides

The oxides of scandium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).



## 25. Silicon Compounds

The only silicon compounds investigated in this study were the carbides, nitrides, and oxides.

### 25.1 Silicon Borides

The borides of silicon were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 25.2 Silicon Carbides

#### Phase Diagram and General Information

Two possible forms of the Si-C phase diagram are shown by Hansen and Anderko.<sup>1</sup> Both diagrams show only a single compound; i. e., SiC. The more recent phase work of Scace and Slack<sup>2</sup> has been reported in the book devoted to silicon carbide by O'Connor and Smiltens.<sup>3</sup> This work also shows only the single compound SiC. Studies of the ternary system Si-B-C by Kalinina and Shamray,<sup>4</sup> and of the Si-C-O system by Krivsky and Schuhmann,<sup>5</sup> have been reported. In addition to the phase diagram by Scace and Slack<sup>2,6</sup> for the binary Si-C system, work has been reported by Dolloff.<sup>7</sup>

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## 25.2.1 Silicon Carbide ( $\text{SiC}_{(s)}$ )

### a. Crystal Structure and Melting Point

A review of the properties of  $\text{SiC}$  and other silicon compounds has been prepared by Berezhnoi.<sup>1</sup> There are believed to be two basic forms of silicon carbide. The stable low-temperature form is considered to be cubic or  $\beta$ - $\text{SiC}$ . According to Taylor and Laidler,<sup>2</sup> the lattice parameter is  $a = 4.3590 \text{ \AA}$ ; and according to Taylor and Jones,<sup>3</sup> at room temperature,  $a = 4.3596 \text{ \AA}$ . The high-temperature form is the hexagonal or  $\alpha$ - $\text{SiC}$ . This form has been found to occur in a large number of additional modifications. For the form containing 6 molecules, Taylor and Laidler<sup>2</sup> found  $a = 3.0817 \text{ \AA}$  and  $c = 15.1183 \text{ \AA}$ . Taylor and Jones<sup>3</sup> found  $a = 3.0806 \text{ \AA}$  and  $c = 15.1173 \text{ \AA}$ . The many forms of  $\alpha$ - $\text{SiC}$  have been explained as due to the ready formation of defects during crystal growth. Only small-energy differences occur since all  $\alpha$ -forms have the same arrangement of neighboring atoms. The differences occur only in the arrangement of atoms in the second and higher coordination. Berezhnoi<sup>1</sup> also notes that 18 hexagonal forms of  $\text{SiC}$  are known. The largest cell contains 393 molecules of  $\text{SiC}$ .

Hansen and Anderko<sup>4</sup> quote the work of Mitchell,<sup>5</sup> who states that there is no limit to the number of possible polymorphs of  $\text{SiC}$ . Hansen and Anderko<sup>4</sup> also list numerous references to crystal-structure data.

Hannay<sup>6</sup> has briefly discussed some of the methods for growing  $\text{SiC}$  crystals and its semiconductor properties. He notes that the cubic ( $\beta$ ) form differs from the hexagonal ( $\alpha$ ) form only by the ordering of the close-packed planes. He cites an energy gap of 2.86 eV for the hexagonal form.

Krishna and Verma<sup>7</sup> have reported a new polytype of  $\text{SiC}$  having 57 layers. They indicate in their paper published in 1962 that over 30 forms of  $\text{SiC}$  have been discovered. They mention five theories proposed to account for the growth of the various polytypes.

From the thermodynamic viewpoint, the energetics involved in the formation of the various  $\alpha$ -forms of  $\text{SiC}$  are undoubtedly very small. Hence, no effort will be made in the present work to account for these differing structures. For the  $\beta \rightarrow \alpha$  transition, there are still no accurate data, but again the thermodynamic quantities are believed

small, but probably appreciably larger than those involved in the various hexagonal ( $\alpha$ ) forms. Whitney<sup>8</sup> has recently noted some difficulties concerned with the  $\beta \rightarrow \alpha$  transformation. Thus, whereas Baumann<sup>9</sup> noted that  $\beta$ -SiC transforms to  $\alpha$ -SiC slowly at 2100°C and rapidly at 2300°C, Scace and Slack<sup>10, 11</sup> found that  $\beta$ -SiC could be heated to 2830°C with no transformation taking place. From the thermodynamic data of Humphrey et al,<sup>12</sup> it is shown that cubic-SiC is stable at least to 1800°K, and hexagonal-SiC is stable at higher temperatures. The difference in heat content ( $H_{1800}^\circ - H_{298}^\circ$ ) of the two forms is only 60 cal/mole, and the entropy difference is only 0.03 e. u. at 298.15°K. The cubic form had a more negative heat of formation at 298.15°K by 1.09 kcal/mole than the hexagonal form. Humphrey et al<sup>12</sup> suggest the difference should be smaller. Davis et al<sup>13</sup> suggest the difference of heats of formation may be only a few hundred calories for  $\alpha$ - and  $\beta$ -SiC. Additional work on the  $\alpha \rightarrow \beta$  transition has been reported by Yasuda.<sup>14</sup>

Because of the uncertainties in the thermodynamic quantities for the  $\alpha$  and  $\beta$  forms of SiC and because of their apparent small magnitude, the present work will tabulate data only for the cubic or  $\beta$ -SiC. It is expected that data for  $\alpha$ -SiC will be in relatively close agreement with that for  $\beta$ -SiC.

According to the work of Scace and Slack,<sup>10, 11</sup> SiC undergoes peritectic decomposition at 2830°C (3103°K). In the present work, this temperature is accepted as a decomposition point. Davis et al<sup>13</sup> also refer to some National Carbon data which indicated a somewhat lower decomposition temperature. Drowart and DeMaria<sup>15</sup> cite works by Kubaschewsk and Evans,<sup>16</sup> and Nowotny et al,<sup>17</sup> which indicate decomposition occurs above 2700°C (2973°K). A very low decomposition temperature reported by Baird and Taylor<sup>18</sup> is considered erroneous because of inaccurate data for SiO<sub>2</sub>.

Silicon carbide (SiC) is considered to be essentially a stoichiometric compound by Lely<sup>19</sup> and Smiltens.<sup>20</sup> Any deviations would be less than 10<sup>-5</sup> atom percent. It was suggested by Brokhin and Funke<sup>21</sup> that at 1900°C a silicon-excess structure may be possible. Wright and Bartels<sup>22</sup> cite the fact that some deviations from stoichiometry are indicated by the film studies of Spitzer et al,<sup>23</sup> and conductivity studies by Kendall.<sup>24</sup>

## b. Thermodynamic Properties

### 1) Low-temperature heat capacities

Kelley and King<sup>25</sup> tabulate  $S_{298.15}^\circ = 3.94 \pm 0.02$  e. u. for hexagonal SiC and  $S_{298.15}^\circ = 3.97 \pm 0.02$  e. u. for cubic SiC. Data for hexa-

gonal SiC had been obtained by Günther,<sup>26</sup> Kelley,<sup>27</sup> Nernst and Schweser,<sup>28</sup> and Humphrey et al.<sup>12</sup> The data for cubic SiC had been obtained by Humphrey et al.<sup>12</sup> Using Humphrey's data, JANAF tables<sup>29</sup> obtained a heat-content value of  $H_{298.15}^\circ - H_0^\circ = 0.781$  kcal/mole, Kelley and King<sup>25</sup> tabulate  $C_p^\circ, 298.15 = 6.42$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> for cubic SiC.

For the present work, the values cited above for cubic SiC based on the Humphrey et al.<sup>12</sup> data, i. e.,  $S_{298.15}^\circ = 3.97$  e. u., and  $H_{298.15}^\circ - H_0^\circ = 0.781$  kcal gfw<sup>-1</sup> have been adopted.

## 2) High-temperature heat content

Kelley<sup>30</sup> cites heat-capacity measurements by Humphrey et al.<sup>12</sup> for the range 298° to 1789°K for hexagonal SiC and 298° to 1693°K for cubic SiC. Other works cited are by Magnus<sup>31</sup> for the range 290° to 1173°K; Michr, Immke, and Kratzert<sup>32</sup> for 290° to 1629°K; and Wiegel<sup>33</sup> for the range 273° to 1224°K.

For hexagonal SiC, Kelley<sup>30</sup> gives:

$$C_p^\circ = 9.93 + 1.92 \times 10^{-3}T - 3.66 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1};$$

and for cubic SiC, he lists:

$$C_p^\circ = 9.97 + 1.82 \times 10^{-3}T - 3.64 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Additional high-temperature heat-capacity data have been obtained by Walker, Ewing, and Miller<sup>34</sup> for the range 30° to 800°C. They also cite work by Maksimenko and Polubelova<sup>35</sup> and Fieldhouse et al.<sup>36</sup> Further work has been reported by Kirillin, Sheindlin, and Chekhovskoy<sup>37</sup> for the range to 2750°C. Their samples contained an excess of carbon which they corrected for by the additivity principle. They apparently did not specify the crystal modification studied. Their values of enthalpy content, corrected to SiC, were about 4 percent lower than the data used by Kelley,<sup>30</sup> and Humphrey et al.<sup>12</sup>

In view of the comparatively good agreement of the data and because of time limitations in making a more-thorough analysis of all the reported data, the data as tabulated by Kelley<sup>30</sup> have been used herein and extrapolated to the decomposition temperature. Since calculations here are being confined to  $\beta$  or cubic-SiC, the equation accepted is

$$C_p^\circ = 9.97 + 1.82 \times 10^{-3}T - 3.64 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

### 3) Heat of formation

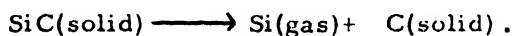
For several years, the calorimetric determinations of the heat of formation of SiC by Humphrey et al<sup>12</sup> have been widely accepted. They have obtained:

$$\Delta H_f^\circ, 298.15, \text{hexagonal SiC} = -12.310 \pm 0.920 \text{ kcal/mole, and}$$

$$\Delta H_f^\circ, 298.15, \text{cubic SiC} = -13.400 \pm 0.920 \text{ kcal/mole.}$$

However, the more recent redetermination of the heat of formation of SiO<sub>2</sub> causes the above values to be made more negative. For example, JANAF tables<sup>29</sup> (1962) revised the heat of formation for cubic SiC to -20.640 kcal/mole. Using values from the present work, the recomputed heat of formation for hexagonal SiC is -20.05 kcal/mole; and for cubic SiC, it is -21.14 kcal/mole.

Several other methods to determine the heat of formation have been used. Vaporization studies have been made by Davis, Anthrop, and Searcy,<sup>13</sup> Grieveson and Alcock,<sup>38</sup> and Drowart et al.<sup>15, 39</sup> The vaporization is considered to proceed via the reaction:



The above three works were recomputed in the present work to yield self-consistent heats of decomposition and heats of formation:

TABLE 53 .

#### HEATS OF FORMATION FOR SiC FROM VAPORIZATION EXPERIMENTS

Reference	$\Delta H_{298.15}^\circ$ , decomposition (kcal/mole)	$\Delta H_{298.15}^\circ$ , formation (kcal/mole)
Davis <u>et al</u> <sup>13</sup>	126.046	-17.639
Grieveson and Alcock <sup>38</sup>	127.517*	-19.110
Drowart and DeMaria <sup>15</sup>	124.325	-15.918

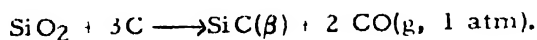
\*Corrections to account for the polyatomic species Si<sub>2</sub>C and SiC<sub>2</sub> from Drowart and DeMaria<sup>15</sup> were made in the Grieveson and Alcock<sup>38</sup> data. Failure to include these corrections would make the  $\Delta H_{298}^\circ$ , sublimation = 122.269 kcal/mole and  $\Delta H_{298.15}^\circ$ , formation = -13.862 kcal/mole.

In making the above calculations, it was assumed that the heat of sublimation of silicon is 108.407 kcal/mole. Since this is subject to an uncertainty of about  $\pm 3$  kcal/mole, it is not to be expected that the heat of formation of SiC will be very precise. In their original publications, Davis *et al*<sup>13</sup> preferred a heat of formation of  $-15 \pm 2$  kcal/mole; and Drowart and DeMaria<sup>15</sup> recommended  $-18 \pm 4$  kcal/mole. Vidale<sup>40</sup> had used a spectro-metric method to study the vaporization and obtained a less-negative heat of formation,  $-12.8$  kcal/mole for  $\alpha$ -SiC, in general agreement with the earlier (uncorrected) values of Humphrey *et al*.<sup>12</sup>

It is likely that a small correction would make this value more negative for  $\beta$ -SiC. Ruff and Konschak<sup>41</sup> also studied the dissociation in the gas phase and obtained a heat of formation of  $-25$  kcal/mole.

Ruff and Grieger,<sup>42</sup> and Ruff,<sup>43</sup> had burned SiC with sodium peroxide in the presence of oxygen to obtain a heat of formation of  $-26.7$  kcal/mole. Droege and Foster<sup>44</sup> had intended to make a similar measurement, but apparently did not obtain any results.

Studies of the reduction of SiO<sub>2</sub> by carbon to form SiC and carbon monoxide have been made by several investigators including Brunner,<sup>45</sup> Baird and Taylor,<sup>18</sup> Kay and Taylor,<sup>46</sup> and Rein and Chipman.<sup>47</sup> Brunner<sup>45</sup> found a heat of formation of  $-36.4$  kcal/mole, and Baird and Taylor<sup>18</sup> found  $-7.7$  kcal/mole. If the Baird and Taylor data are recalculated using their corrected pressures for CO(g) and if the heat of formation for SiO<sub>2</sub> are taken as  $-218.0$  kcal/mole, then a heat of formation of SiC,  $\Delta H_f^{\circ}{}_{298.15} = -16.365$  kcal/mole, is obtained. Similarly, the Kay and Taylor<sup>46</sup> data yield  $\Delta H_f^{\circ}{}_{298.15} = -16.794$  kcal/mole. Rein and Chipman<sup>47</sup> found that  $\Delta F^{\circ} = 0$  at  $1533^{\circ}\text{C}$  ( $1806^{\circ}\text{K}$ ) for the reaction,



Using free-energy functions for CO(g) from JANAF tables<sup>29</sup> and the remainder from the present tabulation, it is found that

$$\Delta(\text{fef}) = \text{fef}_{\text{SiC}} + 2 \text{fef}_{\text{CO}} - \text{fef}_{\text{SiO}_2} - 3 \text{fef}_{\text{C}},$$

$$\text{where fef} = -\left(\frac{F_T^{\circ} - H_{298}^{\circ}}{T}\right),$$

has the value at  $1806^{\circ}\text{K}$ ,

$$\Delta(\text{fef})_{1806} = 82.452 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

Then, since

$$\Delta F^\circ = 0 = \Delta H_{298.15}^\circ - T [\Delta (fef)] ,$$

$$\Delta H_{298.15}^\circ = T [\Delta (fef)] = 1806 \times 82.452,$$

$$= 148,908 \text{ cal/mole} = 148.908 \text{ kcal/mole}.$$

$$\text{Then, } \Delta H_{f, 298.15, \text{ SiC}}^\circ = \Delta H_{298.15}^\circ - 2 \Delta H_{f\text{CO}}^\circ + \Delta H_{f\text{SiO}_2}^\circ,$$

$$= 148.908 - 2(-26.417) + (-218),$$

$$= 148.908 + 52.834 - 218,$$

$$\Delta H_{f, 298.15, \text{ SiC}}^\circ = -16.258 \text{ kcal/mole}.$$

Other studies include those devoted to the solubility of SiC in various metallic solvents. Chipman *et al.*<sup>48</sup> found that the free energy of formation of  $\beta$ -SiC at 1673°K is -10.7 kcal/mole via the solubility in iron. In the present work, this is calculated to give  $\Delta H_{f, 298.15}^\circ = -13.8$  kcal/mole. Kirkwood and Chipman<sup>49</sup> found that the free energy of formation at 1673°K is -10.8 kcal/mole for  $\alpha$ -SiC via solubility in lead, and so  $\Delta H_{f, 298.15}^\circ = -13.9$  kcal/mole. A study of the solubility of  $\beta$ -SiC in molten silver by D'Entremont and Chipman<sup>50</sup> yields  $\Delta H_{f, 298.15}^\circ = -15.8$  kcal/mole. Further studies of the solubility of  $\beta$ -SiC in iron at 1550° to 1600°C (1823° to 1873°K) by Rein and Chipman<sup>47</sup> lead to free energies of formation of -11.6 and -11.0 kcal/mole, respectively. Using the present free-energy functions, values of  $\Delta H_{f, 298.15}^\circ = -15.873$  and -15.712 kcal/mole are calculated.

Another possible way to calculate the heat of formation of SiC is to use the observation by Scafe and Slack<sup>10, 11</sup> that SiC decomposes at 3103°K. Earlier, Davis *et al.*<sup>13</sup> used these data to find a lower limit to the heat of formation. If one assumes that the decomposition yields silicon with activity of unity, a heat of formation of -15.2 kcal/mole is calculated. However, if one assumes that silicon exists in a Raoult-law-type solution, one can estimate its activity as 0.81. Then, the calculation yields a heat of formation at 298.15°K of -16.5 kcal/mole.

Thus, it is seen that there has been a great number of determinations of the heat of formation of SiC. It may be further noted that many originally reported values have needed corrections corresponding to newer data. Smiltens<sup>51</sup> has reviewed the data up to 1960. A summary of the best data obtained during the present analysis is shown in table 54.

TABLE 54

HEATS OF FORMATION FOR SiC AT 298.15°K  
(Values Are Recomputed)

Reference	Type of Experiment	$\Delta H_{f298.15}^{\circ}$ (kcal/mole)
Humphrey <u>et al</u> <sup>12</sup>	Calorimetry	-20.05 $\alpha$ -SiC -21.14 $\beta$ -SiC
Davis <u>et al</u> <sup>13</sup>	Vaporization	-17.639 $\beta$ -SiC
Grieveson and Alcock <sup>38</sup>	Vaporization	-19.110 $\alpha$ -and $\beta$ -SiC
Drowart and DeMaria <sup>15</sup>	Vaporization	-15.918 $\alpha$ -SiC
Vidale <sup>40</sup>	Vaporization	-12.8 <sup>a</sup> $\alpha$ -SiC
Baird and Taylor <sup>18</sup>	SiO <sub>2</sub> -C Equilibria	-16.365
Kay and Taylor <sup>46</sup>	SiO <sub>2</sub> -C Equilibria	-16.794
Rein and Chipman <sup>47</sup>	SiO <sub>2</sub> -C Equilibria	-16.258 $\beta$ -SiC
Chipman <u>et al</u> <sup>48</sup>	Solubility in Fe	-13.8 $\beta$ -SiC
Kirkwood and Chipman <sup>49</sup>	Solubility in Pb	-13.9 $\alpha$ -SiC
D'Entremont and Chipman <sup>50</sup>	Solubility in Ag	-15.8 <sup>b</sup> $\beta$ -SiC
Rein and Chipman <sup>47</sup>	Solubility in Fe	-15.8 $\beta$ -SiC
Scace and Slack <sup>10, 11</sup>	Phase Data	-16.5

<sup>a</sup>The value reported by Vidale<sup>40</sup> was used as reported.

<sup>b</sup>Value reported by authors.<sup>50</sup>

In making a comparison of the data in table 54, it is seen that the data based on the SiO<sub>2</sub> - C - SiC - CO equilibria lead to the best internal agreement. From three independent investigations, the maximum deviation is about 0.5 kcal/mole. The average of these determinations is -16.42 kcal/mole, which is rounded off to give -16.5 kcal/mole. This value is in excellent agreement with the calculations of the phase-diagram data of Scace and Slack,<sup>10, 11</sup> and with the solubility data of Chipman and co-workers.<sup>47-50</sup>



Furthermore, the vaporization data also show general agreement with the chosen value. The calorimetric values of Humphrey<sup>12</sup> are believed to yield too negative a value, indicating the possibility of the same problems as occurred for the combustion of silicon to form SiO<sub>2</sub>. As noted in the section for SiO<sub>2</sub> (section IVB25. 4. 2), the original calorimetric heat-of-formation value for SiO<sub>2</sub> was not negative enough, presumably because of incomplete combustion. It is suggested that the accepted heat of formation, -16.5 kcal/mole, is subject to an uncertainty of about  $\pm 2$  kcal/mole.

In the near future, it is expected that a fluorine combustion of SiC will be completed by Hubbard and co-workers.<sup>52</sup> This could provide a more accurate value than is presently available. Vaporization studies of Fesenko and Bolgar<sup>53</sup> were received too late for analysis here.

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### 25. 3 Silicon Nitrides

#### Phase Data and General Information

No phase diagram is given by Hansen and Anderko<sup>1</sup> for the silicon-nitrogen system. The only compound reported to be formed is  $\text{Si}_3\text{N}_4$ . Samsonov<sup>2</sup> has discussed properties of alloys in the silicon-nitrogen system. Hengge<sup>3</sup> has discussed the preparation of a new silicon subnitride ( $\text{Si}_3\text{N}$ ). Popper and Ruddlesden<sup>4</sup> have reviewed the preparation, properties, and structure of silicon nitride. Forgeng and Decker<sup>5</sup> believe that compounds such as  $\text{SiN}$  and  $\text{Si}_2\text{N}_3$  are not likely. Rabenau<sup>6</sup> has reviewed properties of silicon nitride. At the present time, there appear to be sufficient data to characterize only  $\text{Si}_3\text{N}_4$ .

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#### 25. 3. 1 Silicon Nitride ( $\text{Si}_3\text{N}_4(\text{s})$ )

##### a. Crystal Structure and Melting Point

In their book, Hansen and Anderko<sup>1</sup> suggest that  $\text{Si}_3\text{N}_4$  has an orthorhombic structure,  $a = 13.38 \text{ \AA}$ ,  $b = 8.60 \text{ \AA}$ , and  $c = 7.74 \text{ \AA}$  based on the work of Leslie et al.<sup>2</sup> Additional observations on the more common  $\alpha$  -  $\text{Si}_3\text{N}_4$  (low-temperature form) have been made by Forgeng and Decker<sup>3</sup> and Turkdogan, Bills, and Tippet.<sup>4</sup> Forgeng and Decker have found  $\alpha$  -  $\text{Si}_3\text{N}_4$  and also  $\beta$  -  $\text{Si}_3\text{N}_4$  to be hexagonal. This conclusion is confirmed by Narita and Mori.<sup>5</sup>

Details on the transformation to  $\beta$ - $\text{Si}_3\text{N}_4$  are lacking. Forgeng and Decker<sup>3</sup> indicate that  $\beta$ - $\text{Si}_3\text{N}_4$  is a high-temperature allotropic form of  $\alpha$ - $\text{Si}_3\text{N}_4$ . Attempts to convert  $\beta$ - $\text{Si}_3\text{N}_4$  into  $\alpha$ - $\text{Si}_3\text{N}_4$  have not been successful near 1500°C; either the reaction is monotropic or the rate of transformation is slow.

Pehlke and Elliott<sup>6</sup> have assumed that the  $\alpha \rightarrow \beta$  transformation involves only small changes in enthalpy and entropy. Borgen and Seip<sup>7</sup> found that  $\beta$ - $\text{Si}_3\text{N}_4$  crystals have the same structure as the powder.

Kubaschewski and Evans<sup>8</sup> do not tabulate a melting point for  $\text{Si}_3\text{N}_4$  but indicate that it sublimes. A boiling point of 1900°C (2173°K) is listed.

Brewer et al<sup>9</sup> list a sublimation point for  $\text{Si}_3\text{N}_4$  of 2170°K.

## b. Thermodynamic Properties

### 1) Entropy and heat capacity at 298.15°K

Kelley and King<sup>10</sup> list a single value for the entropy of  $\text{Si}_3\text{N}_4$ ; i. e.,  $S_{298.15}^\circ = 22.8$  e. u. This value has been derived from equilibrium data by Kelley.<sup>11</sup> The equilibrium data used are that of Hincke and Brantley.<sup>12</sup> More recently, Pehlke and Elliott<sup>6</sup> have used their equilibrium data to derive  $S_{298.15}^\circ = 25.6$  e. u. for  $\text{Si}_3\text{N}_4$ . Kubaschewski and Evans<sup>8</sup> tabulate  $S_{298.15}^\circ = 23.0 \pm 2.5$  e. u., and Rossini et al<sup>13</sup> tabulate  $S_{298.15}^\circ = 22.4$  e. u. During the present work, some calculations using the Lindemann equation as described earlier in this report have been made. The assumption has been made that the reported sublimation point of 2170°K is equivalent to a melting point. With this assumption, which essentially provides an upper limit to the thermodynamic functions, the following values have been obtained:  $C_{p,298.15}^\circ = 37.804$  cal degK<sup>-1</sup> gfw<sup>-1</sup>,  $S_{298.15}^\circ = 30.681$  e. u., and  $H_{298.15}^\circ - H_0^\circ = 5.598$  kcal gfw<sup>-1</sup>. If the true melting point is higher (as seems logical), then these latter estimates would be lowered.

For the present work, the data from Pehlke and Elliott<sup>6</sup> are utilized; i. e.,  $C_{p,298.15}^\circ = 30.9$  cal degK<sup>-1</sup> gfw<sup>-1</sup>, and  $S_{298.15}^\circ = 25.6$  e. u. The only value available for  $H_{298.15}^\circ - H_0^\circ = 5.596$  kcal gfw<sup>-1</sup> is retained.

## 2) High-temperature heat content

Kelley<sup>14</sup> tabulates a heat-capacity equation for the range 298.15° to 900°K based on the work of Sato :<sup>15</sup>

$$C_p^\circ = 16.83 + 23.60 \times 10^{-3}T \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation leads to  $C_{p,298.15}^\circ = 23.866 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ , which is rather lower than the value already accepted. Pehlke and Elliott<sup>6</sup> have considered such a value to be too low.

Neel et al<sup>16</sup> have made drop-calorimetry measurements in the range 530° to 2155°K. Their data have been corrected to cgs units and a 298.15°K reference temperature by applying the estimated minor correction of  $H_{298.15}^\circ - H_{273.15}^\circ = 750 \text{ cal gfw}^{-1}$ .

The corrected enthalpy data are shown below.

CONVERTED ENTHALPY DATA FROM NEEL et al<sup>16</sup>

T (°K)	$H_T^\circ - H_{298.15}^\circ$ (cal gfw <sup>-1</sup> )
530.37	4659.4
531.48	5259.6
810.92	15774.4
815.37	16164.1
1084.3	25906.3
1359.8	38378.6
1620.4	46173.1
1909.8	65893.4
2155.4	77974.9

Utilizing  $C_{p,298.15}^{\circ} = 30.9 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  and the Shomate method, the following heat-capacity equation is derived from the Neel et al data:<sup>16</sup>

$$C_p^{\circ} = -3.089 + 3.727 \times 10^{-2}T + 2.033 \times 10^6 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

Because of the unusual form of this equation, it is not given serious consideration.

Two further treatments of the Neel et al data for  $\text{Si}_3\text{N}_4$  have been made. In the first, the two lowest-temperature points (530.37 and 531.48°K) have been excluded from consideration. Then using  $C_{p,298.15}^{\circ} = 30.9 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ , an equation has been derived by the Shomate method:

$$C_p^{\circ} = 17.799 + 0.018842 T + 6.652 \times 10^5 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation fits the measured enthalpies to an accuracy of 6.2 percent or better to the highest temperature of 2155°K. The equation yields

$$C_{p,1000}^{\circ} = 37.306 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

A second treatment of the Neel et al data has been made using all their reported data, but with a value of  $C_{p,298.15}^{\circ} = 23.866 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ . The resulting equation is

$$C_p^{\circ} = 8.7949 + 0.028361 T + 0.58805 \times 10^6 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation yields

$$C_{p,1000}^{\circ} = 37.744 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

The input-enthalpy data are fitted by this equation to 17.3 percent or better. It is thus seen that this latter case gives very poor agreement compared to the previous case.

Also in an attempt to reduce the Pehlke and Elliott<sup>6</sup> estimated data to an equation form, the Shomate treatment has been applied to their tabulated enthalpy values at 600°, 1000°, 1600°, and 2000°K, and using their value of  $C_{p,298.15}^{\circ} = 30.9 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,



the equation obtained is

$$C_p^\circ = 32.074 + 0.0047867 T - 0.23122 \times 10^6 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation fits their tabulated enthalpies to an accuracy of 0.63 percent or better and yields  $C_{p,1000}^\circ = 36.629 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ .

At this point, it may be noted that at 1909°K the experimental Neel et al<sup>16</sup> data yield an enthalpy of  $H_{1909}^\circ - H_{298}^\circ = 65.9 \text{ kcal gfw}^{-1}$ , whereas, interpolating the Pehlke and Elliott estimated data,<sup>6</sup> one obtains  $H_{1909}^\circ - H_{298}^\circ = 59.4 \text{ kcal gfw}^{-1}$ . Thus, the Pehlke and Elliott estimated data are about 9.8 percent lower. Although this is a large error, it is the same order of magnitude as the "fits" to the experimental data of Neel et al.<sup>16</sup>

In view of the considerable uncertainty in the data discussed and for the convenience of remaining consistent with their data, the Pehlke and Elliott data<sup>6</sup> are used herein.

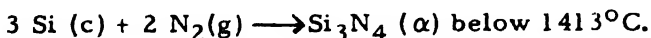
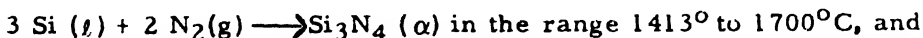
Thus, the equation

$$C_p^\circ = 32.074 + 0.0047867 T - 0.23122 \times 10^6 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}$$

is accepted. Because no definitive data are available on the melting behavior of  $\text{Si}_3\text{N}_4$ , the above equation is extrapolated to 4000°K.

### 3) Heat of formation and vaporization data

Pehlke and Elliott<sup>6</sup> studied the reactions:



From their data, they have deduced that

$$\Delta H_{f298.15}^\circ = -176 \pm 6 \text{ kcal gfw}^{-1} \text{ for } \text{Si}_3\text{N}_4.$$

Sato<sup>15</sup> has obtained

$$\Delta H_{f298.15}^\circ = -163.024 \text{ kcal gfw}^{-1},$$

and Rossini et al<sup>13</sup> have selected

$$\Delta H_{f298.15}^\circ = -179.3 \text{ kcal gfw}^{-1}.$$

Kubaschewski and Evans<sup>8</sup> tabulate

$$\Delta H_{f1298.15}^{\circ} = -179.0 \pm 8.0 \text{ kcal gfw}^{-1}.$$

Dissociation-pressure measurements have been made by Hincke and Brantley,<sup>12</sup> Matignon,<sup>17</sup> Pehlke and Elliott,<sup>6</sup> and Wolff and Alcock.<sup>18</sup> The data by the last workers represent Langmuir data which have not been analyzed in terms of a heat-of-formation value.

Neumann, Kröger, and Kunz<sup>19</sup> analyzed the data of Hincke and Brantley to obtain

$$\Delta H_{f1700}^{\circ} = -176.3 \text{ kcal gfw}^{-1} \text{ for Si}_3\text{N}_4. \text{ This would lead to}$$

$$\Delta H_{f1298.15}^{\circ} \approx -179.0 \text{ kcal gfw}^{-1}.$$

At the present time, it is clear that there is not a very precise value available for the heat of formation of  $\text{Si}_3\text{N}_4$ . Apparently, no combustion measurements have been made. The heat of formation based on dissociation-pressure measurements is made somewhat inaccurate because of uncertainties in free-energy functions, and also because of the poor knowledge of the Si-N phase diagram. An intermediate subnitride as reported by Hengge<sup>20</sup> might make a reevaluation necessary.

Vaporization experiments are considered to yield only elements. However, the gaseous SiN species have been observed in spectra by Thrush.<sup>21</sup>

In the present work for the heat of formation of  $\text{Si}_3\text{N}_4$ , it appears best to adopt the most recent work of Pehlke and Elliott,<sup>6</sup> which agrees well with the Hincke and Brantley<sup>12</sup> data.

Data on the thermal stability of silicon nitride have also been obtained by Kuleshov.<sup>22</sup>

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## 25.4 Silicon Oxides

### Phase Diagrams and General Information

Although the phase  $\text{SiO}_2$  is well known, there appear to be differences of opinion whether other condensed phases exist in the Si-O system. According to a tentative phase diagram by Sosman<sup>1</sup> in the compilation by Levin and McMurdie,<sup>2</sup> the  $\text{SiO}_{(\text{solid})}$  phase has a range of existence at higher temperatures. Schick<sup>3</sup> has reviewed the available data regarding the stability of  $\text{SiO}_{(\text{solid})}$ . Brewer and Edwards<sup>4</sup> and Hoch and Johnston<sup>5</sup> considered  $\text{SiO}_{(\text{s})}$  to be stable above 1450°K and 1573°K, respectively. However, Brady<sup>6</sup> and Brewer and Greene<sup>7</sup> indicate there may be no range of stability. If the latter view is correct, then the often observed SiO films used as optical coatings, etc., may be metastable or may be stabilized by impurities or by their substrates.

Another solid phase recently discussed in the literature is the  $\text{Si}_2\text{O}_3$  phase. Cremer *et al*<sup>8</sup> observed this phase by oxidation of silicon. Dadape and Margrave<sup>9</sup> have also noted this phase.

In the present work, thermodynamic tables have been compiled for  $\text{SiO}_2$  which is well established. However, for the possible SiO and  $\text{Si}_2\text{O}_3$  phases, the available data are too scant to permit reliable tables to be developed.

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## 25. 4. 1 Silicon Monoxide (SiO<sub>(g)</sub>)

### a. Thermodynamic Functions

In 1953, Lagerqvist and Uhler<sup>1</sup> published spectroscopic constants for the ground state ( $^1\Sigma$ ) of the SiO molecule which were in general agreement with the earlier tabulations of Herzberg<sup>2</sup> and Rosen.<sup>3</sup> Barrow and Rowlinson<sup>4</sup> had also accepted the Lagerqvist and Uhler<sup>1</sup> data for the ground state. Barrow and Rowlinson<sup>4</sup> further indicated that a  $^3\Pi_r$  state for SiO was expected to be analogous to the upper state of the Cameron bands in CO. In 1961, Verma and Mulliken<sup>5</sup> observed a  $^1\Sigma - ^3\Pi_r$  spectrum and obtained spectroscopic constants for the  $^3\Pi_r$  state. Recently, James<sup>6</sup> suggested an explanation for the forbidden spectrum observed by Verma and Mulliken.<sup>5</sup>

For the purpose of preparing thermodynamic tables, the data of Lagerqvist and Uhler<sup>1</sup> for the ground state and of Verma and Mulliken<sup>5</sup> for the next higher state have been accepted. Because the energy level of the  $^3\Pi_r$  state is only inaccurately known and since the other states are much higher, the additional higher states have been ignored.

In the case of the ground state, the spectroscopic constants from Lagerqvist and Uhler<sup>1</sup> were utilized directly. However for the  $^3\Pi_r$  excited state observed by Verma and Mulliken,<sup>5</sup> there were no data for the electronic energy level or for the vibrational frequency. The latter authors had indicated that the level is at about 4 e. v. ( $32264\text{ cm}^{-1}$ ) above the ground state on their figure but did not give a precise figure. For the present case, this level was estimated by analogy to CO, using data from Herzberg<sup>2</sup> for CO, and from Lagerqvist and Uhler<sup>1</sup> for SiO.

From these sources, the term values are  $T_e(a^3\Pi(\text{CO})) = 48687.55\text{ cm}^{-1}$ ,  $T_e(A^1\Pi(\text{CO})) = 65074.8\text{ cm}^{-1}$ , and  $T_e(A^1\Pi(\text{SiO})) = 42640.4\text{ cm}^{-1}$ .

Then,  $T_e(a^3\Pi(\text{SiO}))$  is evaluated as

$$\begin{aligned} T_e(a^3\Pi(\text{SiO})) &= 42640.4 \times \frac{48687.55}{65074.8} \\ &= 31902.6\text{ cm}^{-1} \end{aligned}$$

The value of  $T_e$  thereby calculated is rounded off to give as the energy level (E) accepted in the present calculations,  $E = 32000\text{ cm}^{-1}$ .

To estimate  $\omega_e$  for the  $a^3\Pi$  state, the analogy with the CO molecule is also used.

TABLE 55

## VARIOUS COMBINATIONS OF BASIC INPUT DATA FOR SILICON MONOXIDE (gas)

HS16 (Case 3) Ground State (Lagerqvist and Uhler<sup>1</sup> Data);<sup>3</sup> $\pi_r$  Verma and Mulliken<sup>5</sup> (These Data Used  
for Preparing Tables in Present Report)

$E \text{ (cm}^{-1}\text{)}$	0.0	32000
$g$	1.0	6.0
$\omega_e \text{ (cm}^{-1}\text{)}$	1241.44	1000
$\omega_e x_e \text{ (cm}^{-1}\text{)}$	5.92	6.0
$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.0	0.0
$\alpha_e \text{ (cm}^{-1}\text{)}$	0.00508	0.0
$\gamma_e \text{ (cm}^{-1}\text{)}$	0.0	0.0
$B_e \text{ (cm}^{-1}\text{)}$	0.72729	0.67656
$D_e \text{ (cm}^{-1}\text{)}$	$1.02 \times 10^{-6}$	$1.4 \times 10^{-6}$

HS10 Ground State Only  
(Herzberg<sup>2</sup> Data)HS18 (Case 1) Ground State Only  
(Lagerqvist and Uhler<sup>1</sup> Data)

$E \text{ (cm}^{-1}\text{)}$	0.0	$E \text{ (cm}^{-1}\text{)}$	0.0
$g$	1.0	$g$	1.0
$\omega_e \text{ (cm}^{-1}\text{)}$	1242.03	$\omega_e \text{ (cm}^{-1}\text{)}$	1241.44
$\omega_e x_e \text{ (cm}^{-1}\text{)}$	6.047	$\omega_e x_e \text{ (cm}^{-1}\text{)}$	5.92
$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.00329	$\omega_e y_e \text{ (cm}^{-1}\text{)}$	0.0
$\alpha_e \text{ (cm}^{-1}\text{)}$	0.00494	$\alpha_e \text{ (cm}^{-1}\text{)}$	0.00508
$\gamma_e \text{ (cm}^{-1}\text{)}$	$2.2399 \times 10^{-5}$	$\gamma_e \text{ (cm}^{-1}\text{)}$	0.0
$B_e \text{ (cm}^{-1}\text{)}$	0.7263	$B_e \text{ (cm}^{-1}\text{)}$	0.72729
$D_e \text{ (cm}^{-1}\text{)}$	$9.934 \times 10^{-7}$	$D_e \text{ (cm}^{-1}\text{)}$	$1.02 \times 10^{-6}$

$$\begin{aligned}
 \omega_e(\text{SiO}, a^3\pi) &= \omega_e(\text{CO}, a^3\pi) \times \frac{\omega_e(\text{SiO}, ^1\Sigma)}{\omega_e(\text{CO}, ^1\Sigma)} \\
 &= 1739.25 \times \frac{1241.44}{2170.21} \\
 &= 994.915 \text{ cm}^{-1}
 \end{aligned}$$

This value is then rounded off to give  $\omega_e = 1000 \text{ cm}^{-1}$  for the  $a^3\pi$  state of SiO.

The final selected constants used for calculating the accepted thermodynamic table are shown in table 55 as HS16. Some additional cases are also given in this table to illustrate the effects of changing input variables. The results at selected temperatures are shown in table 56. It is to be noted that the change in entropy at 6000°K for the cases of considering only the ground state (HS10 or HS18) and for considering both lowest states (HS16) amounts to only 0.063 to 0.068 e. u. In view of the uncertainties of the data for the  $a^3\pi$  state itself and because of the small effect of higher states, these higher states have not been considered in the present calculations. The results obtained for SiO(g) in the present calculations are believed to be fairly reliable, and entropy and free-energy function values to 6000°K should probably be good to  $\pm 0.1$  e. u.

TABLE 56

SUMMARY OF DATA OBTAINED FROM VARIOUS CASES FOR  
SILICON MONOXIDE (gas)  
(All Quantities in cal deg K<sup>-1</sup> gfw<sup>-1</sup>)

Case \ Temperature	298.15°K		3000°K		6000°K	
	C <sub>p</sub> <sup>°</sup> cal/deg K gfw	S <sup>°</sup> e. u.	C <sub>p</sub> <sup>°</sup> cal/deg K gfw	S <sup>°</sup> e. u.	C <sub>p</sub> <sup>°</sup> cal/deg K gfw	S <sup>°</sup> e. u.
HS16 (Present Report)	7.146	50.544	9.043	69.753	9.699	76.163
HS10	7.146	50.546	9.039	69.752	9.261	76.095
HS18	7.146	50.544	9.042	69.752	9.273	76.100

## b. Uncertainties

Uncertainties of the thermodynamic functions for  $\text{SiO}_{(g)}$  have been estimated through considerations of the type given in table 56. That is, by noting the effects of changes in the input data on the resultant output, an estimate of the probable accuracy can be made.

## c. Heat of Formation

In recent years, there have been several studies of the vaporization of  $\text{SiO}_2$ . Since  $\text{SiO}_2$  vaporizes into  $\text{SiO}_{(g)}$ , it is possible to derive heat-of-formation data therefrom. A review of earlier  $\text{SiO}_2$  vaporization data has been given by Schick.<sup>7</sup> More recently, Wise et al<sup>8</sup> have reviewed earlier and later work. Based on the newer heat-of-formation values for  $\text{SiO}_2$ ,<sup>8-13</sup> they have derived a heat of formation of  $\text{SiO}_{(g)}$ ,  $\Delta H_{f298.15}^\circ = -24.04 \pm 0.45 \text{ kcalgfw}^{-1}$ .

Some vaporization studies are presented elsewhere.<sup>14-23</sup> At the time of report preparation, it was not possible to do a complete self-consistent analysis of all the vaporization data available for  $\text{SiO}_{(g)}$ . As an interim measure, the most recent analysis by Wise et al<sup>8</sup> was accepted, thus giving  $\Delta H_{\text{formation}}^\circ, \text{SiO}_{(g)}, 298.15 = -24.04 \pm 0.45 \text{ kcalgfw}^{-1}$ .

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## 25.4.2 Silicon Dioxide ( $\text{SiO}_2(\text{s}, \text{l})$ )

### a. Crystal Structure, Transition Points, and Melting Point

Silica and the silicates are compounds of tremendous technical value. Hence, there is a voluminous literature devoted to these materials. In spite of this great amount of work, there are still many questions regarding its physical and chemical properties.

Schick<sup>1</sup> has reviewed much of the thermodynamic data for pure  $\text{SiO}_2$ . He lists the following phases as the stable ones:

Form	Temperature Range of Stability (°C)
silica glass	above 1728
$\beta$ -cristobalite	1470 to 1728
$\beta$ -tridymite	870 to 1470*
$\beta$ -quartz	573 to 870
$\alpha$ -quartz	up to 573

\*Schick notes that questions as to the stability of tridymite were raised by Holmquist<sup>2</sup> and Tokuda.<sup>3</sup>

According to the original classic Fenner<sup>4</sup> investigation of 1913, several crystalline forms of  $\text{SiO}_2$  with different ranges of stability were recognized. Fenner found that  $\alpha$ -quartz is stable to 870°C (1143°K); tridymite is stable from 870 to 1470°C (1143 to 1743°K), and cristobalite is stable from 1743°K to the melting point.

Brewer<sup>5</sup> considered that  $\alpha$ -quartz (hexagonal<sup>1</sup>) is stable up to 848°K where it transforms to  $\beta$ -quartz (hexagonal). The latter is stable up to 1140°K. Above 1140°K, Brewer states that  $\beta$ -quartz transforms slowly into the more stable  $\beta$ -tridymite (hexagonal). He considers  $\beta$ -tridymite the stable form to 1743°K where  $\beta$ -cristobalite (cubic) becomes stable.

Mosesman and Pitzer<sup>6</sup> have summarized the important phases and discussed their stability. Sosman<sup>7</sup> has presented a tentative phase diagram for the Si- $\text{SiO}_2$  system. The results of his work have been compiled by Levin and McMurdie.<sup>8</sup> According to that work,  $\alpha$  (low) quartz is stable up to 573°C;  $\beta$  (high) quartz is stable from 573 to 867°C; tridymite(I) is stable from 867 to 1470°C;  $\beta$  (high) cristobalite is stable from 1470 to 1723°C. Above 1723°C, the liquid or glass form of  $\text{SiO}_2$  becomes the stable condensed phase.

Holmquist<sup>9</sup> has obtained results which indicate that tridymite is not a stable form of SiO<sub>2</sub>, but rather a binary incongruently melting phase. He feels that tridymite can only be stabilized by the addition of impurities such as alkali oxides. According to Holmquist,<sup>9</sup> quartz and cristobalite are the only two stable crystalline forms of SiO<sub>2</sub>. The quartz-cristobalite transformation temperature is considered to be 1025 ± 25°C (1298 °K).

Chaklader<sup>10</sup> has studied the kinetics of the quartz-cristobalite transformation at 1560°C. Arnold<sup>11</sup> has presented structural data for the quartzes. Mackenzie<sup>12</sup> found that the melting point of the quartz phase is in the range 1673 to 1723°K. Schick<sup>1</sup> noted that the following melting points had been reported:

Form	Melting Point (°C)
cristobalite	1728
tridymite	1680
quartz	1610

Floerke<sup>13</sup> presented a provisional phase diagram which excluded the tridymite phase in agreement with Holmquist.<sup>9</sup>

In view of the findings of Holmquist<sup>9</sup> and Floerke,<sup>13</sup> we revise the older work and do not consider tridymite as a stable phase. The forms accepted are shown below.

#### STABLE FORMS OF SiO<sub>2</sub> ACCEPTED IN PRESENT WORK

Form	Temperature Range of Stability (°K)
$\alpha$ -quartz (hexagonal)	298.15 to 848
$\beta$ -quartz (hexagonal)	848 to 1298
$\beta$ -cristobalite (cubic)	1298 to 1996
liquid SiO <sub>2</sub> (glass)	1996 to 6000*

\*According to Schick,<sup>1</sup> SiO<sub>2</sub> boils at 3070°K. Hence, the liquid phase is metastable above this temperature at 1 atm.

In addition to the phases considered to be the stable ones, as shown above, there exist phases which are metastable under ordinary conditions. We have adopted this viewpoint for tridymite. A high-pressure phase of SiO<sub>2</sub> named coesite has also not been considered herein. This phase has a monoclinic, pseudo-hexagonal unit cell according to Anikina.<sup>14</sup> The atomic packing is much denser in coesite than in quartz. Some studies on the conversion of quartz to coesite at high pressure have been made by Dacheville and Roy<sup>15</sup> and Boyd and

England.<sup>16</sup> Other metastable phases such as  $\alpha$ -cristobalite are also not considered in the present work.

The  $\alpha$  -  $\beta$  quartz transition at 848°K is in good agreement with a value of 846°K found by Keith and Tuttle.<sup>17</sup> The temperature 1298°K for the transition  $\beta$ -quartz  $\rightarrow$   $\beta$ -cristobalite is in agreement with Mosesman and Pitzer.<sup>6</sup> The melting point of 1996°K is in good agreement with a value of 2001°K tabulated by Rossini *et al*<sup>18</sup> and 1996°K tabulated by Levin and McMurdie,<sup>8</sup> and Sosman.<sup>7</sup>

## b. Thermodynamic Properties

### 1) Low-temperature heat capacities

Kelley and King<sup>19</sup> tabulate heat-capacity data up to 298.15°K for  $\alpha$ -quartz (the stable form) as well as for several of the metastable forms. For  $\alpha$ -quartz, Anderson<sup>20</sup> obtained data in the range 53 to 297°K, Nernst<sup>21</sup> in the range 25 to 233°K, and Wietzel<sup>22</sup> in the range 71 to 89°K. From analysis of these sources, Kelley and King<sup>19</sup> obtained  $S_{298.15}^\circ = 10.00 \pm 0.10$  eu. This value is also utilized in the present work.

Since Kelley and King<sup>19</sup> do not tabulate values of  $H_{298.15}^\circ - H_0^\circ$ , it has been necessary to recompute this value. Unfortunately, the exact "weighting" of data used by Kelley and King<sup>19</sup> is not known. In the present case, the integration has been performed by using the data given by Anderson.<sup>20</sup> It is expected that negligible inconsistency is introduced, since Anderson's value of  $S_{298.15}^\circ$  is in excellent agreement with the data from Kelley and King.<sup>19</sup> Thus, the present integration of Anderson's data yielded  $H_{298.15}^\circ - H_0^\circ = 1.664$  kcal gfw<sup>-1</sup> and  $S_{298.15}^\circ = 10.084$  eu. These results included extrapolated contributions of  $S_{53.4}^\circ = 0.862$  eu. and  $H_{53.4}^\circ - H_0^\circ = 0.031$  kcal gfw<sup>-1</sup>. The extrapolations were based on the functions proposed by Anderson.<sup>20</sup>

Additional low-temperature heat capacity data have been obtained by Westrum.<sup>23, 24</sup> These data were not available at time of report preparation and are not utilized herein.

For the present work, we have utilized the Kelley and King<sup>19</sup> value of  $S_{298.15}^\circ = 10.00 \pm 0.10$  e.u., and our calculated value of  $H_{298.15}^\circ - H_0^\circ = 1.664$  kcal gfw<sup>-1</sup>.

### 2) High-temperature heat content

Kelley<sup>25</sup> has tabulated heat-content data for quartz, cristobalite, tridymite, and vitreous SiO<sub>2</sub>. For  $\alpha$ -quartz he gives:

$$C_p^\circ = 11.22 + 8.20 \times 10^{-3}T - 2.70 \times 10^5 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1} \text{ for } 298.15^\circ\text{K} \leq T \leq 848^\circ\text{K}.$$

The heat of transition at 848°K to yield  $\beta$ -quartz is given as 290 cal gfw<sup>-1</sup>.

From 848 to 1298°K, we have adopted the Kelley<sup>25</sup> equation for  $\beta$ -quartz; i. e. :

$$C_p^\circ = 14.41 + 1.94 \times 10^{-3}T \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

At 1298°K for the transition from  $\beta$ -quartz to  $\beta$ -cristobalite, we cannot use the tabulated Kelley data since he does not give data for this transition. In the present instance, these data have been estimated using data compiled by Rossini et al.<sup>18</sup> The latter give:

$\beta$ -quartz  $\longrightarrow$   $\beta$ -tridymite,  $T = 1140^\circ\text{K}$ ;  $\Delta H^\circ = 0.120 \text{ kcal}$ ;  $\Delta S^\circ = 0.11 \text{ e.u.}$ ,

$\beta$ -tridymite  $\longrightarrow$   $\beta$ -cristobalite,  $T = 1743^\circ\text{K}$ ;  $\Delta H^\circ = 0.05 \text{ kcal}$ ;  $\Delta S^\circ = 0.03 \text{ e.u.}$ ,

adding

$\beta$ -quartz  $\longrightarrow$   $\beta$ -cristobalite,  $\Delta S^\circ = 0.14 \text{ e.u.}$

From this estimated entropy of transition, we calculate at 1298°K,  $\Delta H^\circ = 181.7 \text{ cal gfw}^{-1}$  which is rounded off to give for the present case

$$\Delta H^\circ_{\beta\text{-quartz} \longrightarrow \beta\text{-cristobalite}, 1298^\circ\text{K}} = 180 \text{ cal gfw}^{-1}.$$

Above 1298°K for  $\beta$ -cristobalite, the heat capacity equation of Kelley<sup>25</sup> is used; i.e. :

$$C_p^\circ = 14.40 + 2.04 \times 10^{-3}T \text{ cal deg K}^{-1} \text{ gfw}^{-1} \text{ for } 1298^\circ\text{K} \leq T \leq 1996^\circ\text{K}.$$

At the melting point of 1996°K, the average value of 2100 cal gfw<sup>-1</sup> for the heat of fusion from Schick<sup>1</sup> was used.

The heat capacity of liquid SiO<sub>2</sub> was estimated by Schick to be  $21.66 \pm 1.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  and was utilized herein.

### 3) Heat of formation

For several years, the combustion data of Humphrey and King<sup>26</sup> had been generally accepted as the most accurate value for the heat of formation of SiO<sub>2</sub>. For  $\alpha$ -quartz they obtained  $\Delta H_{f298.15}^{\circ} = -210.260 \pm 0.270$  kcal gfw<sup>-1</sup>. Even earlier, Roth and Troitsch<sup>27</sup> obtained  $-208.3 \pm 0.6$  kcal gfw<sup>-1</sup>, and Roth and Becker<sup>28</sup> found  $-205.6 \pm 0.3$  kcal gfw<sup>-1</sup>.

However, Chipman<sup>29</sup> noted discrepancies in the heat-of-formation data for SiO<sub>2</sub> and indicated that it should be 3 to 8 kcal gfw<sup>-1</sup> more negative than the Humphrey and King<sup>26</sup> value. His predictions have been amply confirmed by the works of Golutvin,<sup>30</sup> Wise et al,<sup>31,32</sup> Good et al,<sup>33</sup> and Cochran and Foster.<sup>34</sup> A list of the reported values is given below:

$\Delta H_{f298.15}^{\circ}$ (kcal gfw <sup>-1</sup> )	Reference
-205.6	Roth and Becker <sup>28</sup>
-208.3	Roth and Troitsch <sup>27</sup>
-210.26	Humphrey and King <sup>26</sup>
-219 $\pm$ 1	Golutvin <sup>30</sup>
-217.75 $\pm$ 0.34	Wise <u>et al</u> (1962) <sup>31</sup>
-217.72 $\pm$ 0.34	Wise <u>et al</u> (1963) <sup>32</sup>
-217.5 $\pm$ 0.5	Good <u>et al</u> <sup>33</sup>
-215.8 $\pm$ 2.2	Cochran and Foster <sup>34</sup>

In analyzing the above data it is seen that the works of Golutvin,<sup>30</sup> Wise et al,<sup>31,32</sup> and Good et al,<sup>33</sup> agree very well with each other. Furthermore, all of these experiments utilized different calorimetric techniques. Golutvin<sup>30</sup> used direct oxygen-bomb calorimetry; Wise et al<sup>31,32</sup> burned quartz in fluorine; and Good et al<sup>33</sup> burned elemental silicon with oxygen and aqueous HF to form fluosilicic acid. In the present work, these three determinations have been considered to be the most precise. A final selected value of  $\Delta H_{f298.15}^{\circ} = -218.0$  kcal gfw<sup>-1</sup> was chosen as the heat of formation of SiO<sub>2</sub> ( $\alpha$ -quartz) which "fits" the estimated uncertainties of

all three investigations. It may be noted that this is in excellent agreement with the average value  $-218.07 \text{ kcal gfw}^{-1}$  of the three separate values from Golutvin,<sup>30</sup> Wise et al,<sup>32</sup> and Good et al.<sup>33</sup> It would appear probably that the chosen value is good to  $\pm 0.5 \text{ kcal gfw}^{-1}$ .

#### 4) Vaporization studies

Schick<sup>1</sup> has reviewed much of the data on the vaporization of  $\text{SiO}_2$ . Under neutral conditions, it is expected that the following reaction is most important:



In the above reaction,  $\text{SiO}_2$  is considered to be solid below  $2000^\circ\text{K}$  and liquid above  $2000^\circ\text{K}$ ;  $\text{SiO}(\text{g})$  is the most important gaseous species. However,  $\text{SiO}_2(\text{g})$  is also present, although in smaller amounts.

A number of vaporization studies have been performed. Grube and Speidel,<sup>35</sup> Tombs and Welch,<sup>36</sup> and Ramstad and Richardson<sup>37</sup> have studied reduction of  $\text{SiO}_2$  with hydrogen. Reduction of  $\text{SiO}_2$  with silicon has been studied by Schafer and Hornle,<sup>38</sup> Gel'd and Kochnev,<sup>39</sup> Porter et al,<sup>40</sup> Gunther,<sup>41</sup> Tombs and Welch,<sup>36</sup> and Ramstad and Richardson.<sup>37</sup>

Vaporization of  $\text{SiO}_2$  under essentially neutral conditions has been performed by Brewer and Mastick,<sup>42</sup> Porter et al,<sup>40</sup> and Nesmeyanov and Firsova.<sup>43, 44, 45</sup>

Additional data on the vaporization of  $\text{SiO}_2$  have been given in reviews by Schick,<sup>1</sup> Ackermann and Thorn,<sup>46</sup> Brewer and Edwards,<sup>47</sup> and Wise et al.<sup>32</sup> Properties of  $\text{SiO}(\text{g})$  and  $\text{SiO}_2(\text{g})$  are discussed separately in sections devoted to these species.

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### 25.4.3 Silicon Dioxide ( $\text{SiO}_2(\text{g})$ )

#### a. Thermodynamic Functions

Experimental spectroscopic data to enable calculation of thermodynamic properties for  $\text{SiO}_2$  are not available. However, several estimates of its properties have been made.

Brewer and Rosenblatt<sup>1</sup> considered  $\text{SiO}_2$  to have a  $^1\Sigma$  electronic state and a linear structure. Vibrational frequencies were estimated, but not tabulated by them. Schick<sup>2</sup> also assumed  $\text{SiO}_2$  to be linear and estimated the vibrational frequencies to be  $767\text{ cm}^{-1}$ ,  $382\text{ cm}^{-1}$  (mult = 2) and  $1340\text{ cm}^{-1}$ . JANAF<sup>3</sup> utilized data estimated by Gordon<sup>4</sup> to give frequencies of  $885\text{ cm}^{-1}$ ,  $378\text{ cm}^{-1}$  (mult = 2), and  $1295\text{ cm}^{-1}$ .

For the present work, a procedure analogous to that used by Brewer and Rosenblatt<sup>1</sup> has been followed. An ionic model has been assumed. For this model, the energy level of the cation is needed. The levels of  $\text{Si}^{+4}$  are tabulated in Moore.<sup>5</sup> It is noted that the ground state is  $^1S$  which corresponds to a  $^1\Sigma$  electronic state for  $\text{SiO}_2(\text{g})$ . No other electronic levels are of importance.

The structure of  $\text{SiO}_2$  is assumed to be linear, O-Si-O. It thus belongs to the point group  $D_{\infty h}$  with symmetry number 2.

Intruclear distances in the dioxide have been considered to be the same as for the monoxide. Brewer and Rosenblatt had also made the same assumption. Sutton<sup>6</sup> tabulates  $r_e = 1.509\text{ \AA}$  which is utilized in the present calculations.

A moment of inertia,  $I = 2 m_O r_e^2 = 12.09767 \times 10^{-39}\text{ gm-cm}^2$ , and a rotational constant,  $B_e = 0.23135\text{ cm}^{-1}$ , are then calculated.

Vibrational frequencies were estimated by a valence bond calculation. It was assumed that the stretching force constant  $k_1$  has the same value as exists in the monoxide. The ratio of bending force constant  $k_2/l^2$  to the stretching force constant  $k_1$  was assumed to be 0.034 rather than 0.0336 as used by Brewer and Rosenblatt.<sup>1</sup> The difference is trivial but the choice of 0.034 is consistent with other calculations on this project. The vibrational frequency for  $\text{SiO}(\text{g})$  accepted on this project of  $1241.44\text{ cm}^{-1}$  from Lagerqvist and Uhler<sup>7</sup> was utilized in the calculations. The results gave

$$\omega_1 = 990.9\text{ cm}^{-1}$$

$$\omega_2 = 377.9\text{ cm}^{-1} \text{ (mult = 2)}$$

$$\omega_3 = 1449.3\text{ cm}^{-1}$$

In the above, the frequency  $\omega_2$  is doubly degenerate.

#### b. Heat of Formation

JANAF<sup>3</sup> lists a heat of formation for  $\text{SiO}_2(\text{g})$  of  $\Delta H_{f,298.15}^\circ = -73.9$  kcal/mole. From the vaporization data of Porter, Chupka, and Inghram,<sup>8</sup> Schick<sup>2</sup> calculated an average third-law heat of sublimation of  $\Delta H_{298.15}^\circ = 141.169$  kcal/mole. Assuming the heat of formation of  $\text{SiO}_2$  to be  $-218.0$  kcal/mole as discussed in a separate section from the works of Wise et al,<sup>9</sup> Chipman,<sup>10</sup> Golutvin,<sup>11</sup> Wise et al,<sup>12</sup> Good et al,<sup>13</sup> and Cochran and Foster,<sup>14</sup> a heat of formation of  $\text{SiO}_2(\text{g})$  is calculated as  $\Delta H_{f,298.15}^\circ = -76.831$  kcal/gfw. Brewer and Rosenblatt,<sup>1</sup> in their analysis, obtained heats of sublimation at  $298.15^\circ\text{K}$  of  $135$  kcal/mole and  $137$  kcal/mole. The average is  $136$  kcal/mole which thus leads to a heat-of-formation value of

$$\Delta H_{f,298.15}^\circ, \text{SiO}_2(\text{g}) = -82.0 \text{ kcal/gfw.}$$

In the present work, the original vapor pressure data of Porter et al<sup>8</sup> was used to calculate an average heat of sublimation of  $\text{SiO}_2(\text{s})$  at  $298.15^\circ\text{K}$  of  $\Delta H_{298.15}^\circ = 140.567$  kcal gfw<sup>-1</sup>. The results are shown in table 57. Combining with the heat of formation of  $\text{SiO}_2$  accepted in this work,  $\Delta H_{f,298.15}^\circ, \text{SiO}_2(\text{solid}) = -218.0$  kcal gfw<sup>-1</sup>, a heat of formation for  $\text{SiO}_2(\text{g})$  is calculated as

$$\Delta H_{f,\text{SiO}_2(\text{g}); 298.15}^\circ = -218.0 + 140.567$$

$$\Delta H_{f,\text{SiO}_2(\text{g}); 298.15}^\circ = -77.433 \text{ kcal gfw}^{-1}.$$

TABLE 57

ANALYSIS OF PARTIAL PRESSURE DATA AS REPORTED  
BY PORTER et al<sup>8</sup> FOR REACTION  
 $\text{SiO}_2(\text{solid}) \longrightarrow \text{SiO}_2(\text{gas})$

T (°K)	P <sub>SiO<sub>2</sub>(g)</sub> (atm)	$\left( \frac{F_T^\circ - H_{298}^\circ}{T} \right)_{\text{SiO}_2(\text{solid})}$ (cal degK <sup>-1</sup> gfw <sup>-1</sup> )	$\left( \frac{F_T^\circ - H_{298}^\circ}{T} \right)_{\text{SiO}_2(\text{g})}$ (cal degK <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_{298.15}^\circ$ (kcal gfw <sup>-1</sup> )
1800	$1.6 \times 10^{-8}$	24.308	66.558	140.260
1900	$1.0 \times 10^{-7}$	25.062	67.175	140.873
Average				140.567

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## 26. Strontium Compounds

The only strontium compounds investigated in this study were the oxides.

### 26.1 Strontium Borides

The borides of strontium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 26.2 Strontium Carbides

The carbides of strontium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 26.3 Strontium Nitrides

The nitrides of strontium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 26.4 Strontium Oxides

In this study, detailed analyses of strontium oxides were made for  $\text{SrO}_{(s,l)}$  and  $\text{SrO}_{(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 26.4.1 Strontium Oxide ( $\text{SrO}_{(s,l)}$ , $\text{SrO}_{(g)}$ )

##### a. Condensed Phases

For the calculation of the  $\Delta H_f^\circ$ ,  $\Delta F_f^\circ$ , and  $\log_{10} K_p$  of the condensed phases of  $\text{SrO}$ ,  $\Delta H_{f298}^\circ$  was taken to be -141.100 kcal/gfw from NBS Circular 500.<sup>1</sup> An uncertainty of  $\pm 2.000$  kcal/gfw was assigned to  $\Delta H_{f298}^\circ$ . Other data previously used for a hand calculation<sup>2</sup> were retained, and the thermodynamic functions were recomputed by machine.

##### b. Gaseous Strontium Oxide

The thermodynamic functions for  $\text{SrO}_{(g)}$  were recalculated with an assumed  $^3\Sigma$  ground state. (The reasons for this are discussed in the sections on  $\text{MgO}$  and  $\text{CaO}$ .) For  $\text{SrO}_{(g)}$ , the multiplicity of the lowest observed  $^1\Sigma$  state was increased to 3; however, that of the other singlet states was unchanged. This was equivalent to placing the start of the singlet system approximately  $10,000 \text{ cm}^{-1}$  above the assumed triplet

ground state. No other triplet states of greater electronic energy were assumed to exist. Spectroscopic constants used in the calculation were given previously.<sup>2</sup>

As also noted in the cases of MgO(g) and CaO(g), a discrepancy existed between the thermochemical and spectroscopic values of the dissociation energy of SrO(g). In all these cases, it had been generally assumed that the spectroscopic values were too low because the lowest lying singlet states to which they referred were not the ground states. However, because of experimental difficulties, even the thermochemical experiments did not give unambiguous results for SrO(g). The thermochemical dissociation energy values at 0°K, as derived from the various thermochemical experiments, had been reviewed by the following authors who preferred the indicated values:

Source	$D_0^\circ$
	kcal/gfw
Brewer <sup>3</sup>	111 ± 4
Brewer <sup>4</sup>	83 ± 5
Gaydon <sup>5</sup>	106 ± 12
Ackermann, Thorn, and Winslow <sup>6</sup>	111

For the present compilation, a dissociation energy at 0°K of 110 kcal/gfw was selected. This value was derived from a partial pressure of SrO(g) of  $1.06 \times 10^{-10}$  atm at 1500°K and appropriate thermodynamic functions for SrO, O, and Sr from the present compilation. The indicated partial pressure of SrO(g) at 1500°K was calculated by Ackermann and Thorn<sup>7</sup> from the vapor-pressure measurements of Moore, Allison, and Struthers.<sup>8</sup> From flame studies, Lagerqvist and Huldt<sup>9</sup> determined  $D_0^\circ$  to be 106 kcal/gfw, and Veits and Gurvich<sup>10</sup> reported the value to be 111 kcal/gfw.

A value for the  $\Delta H_{f298}^\circ$  of SrO(g) equal to -12.300 kcal/gfw was calculated from the adopted  $D_0^\circ$  and appropriate thermodynamic functions for SrO(g), Sr, and O from the present compilation. An uncertainty of ± 10 kcal/gfw was assigned to  $\Delta H_{f298}^\circ$ .

The sum of the partial pressures of all vaporizing species was calculated to equal 1 atm at 4500°K. Vaporization was found by calculation to proceed principally to undissociated SrO(g); and at the vaporization temperature, the partial pressure of SrO(g) was calculated to be 0.78 atm.

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## 27. Tantalum Compounds

Selected borides, carbides, nitrides, and oxides of tantalum were investigated.

### 27.1 Tantalum Borides

#### General Information

The tantalum-boron system is discussed by Hansen and Anderko<sup>1</sup> but no phase diagram is given. The diboride  $TaB_2$  appears to be the most refractory compound formed in this system. Other possible borides include:  $Ta_3B$ ,  $Ta_2B$ ,  $TaB$ , and  $Ta_3B_4$ . Further data have been given by Leitnaker,<sup>2</sup> Leitnaker, Bowman, and Gilles,<sup>3, 4</sup> Nowotny and Wittmann,<sup>5</sup> and Nowotny et al.<sup>6</sup> The work by Nowotny et al.<sup>6</sup> is the most comprehensive and covers the entire Ta-B phase diagram, whereas the work by Leitnaker and co-workers<sup>2, 3, 4</sup> is restricted to the Ta-TaB region. Even in this region there were several areas of conflict.

Further indication of the complexity of the Ta-B system is given by the vaporization studies of Walker and co-workers.<sup>7, 8</sup> Earlier phase work has been reported by Brewer et al.<sup>9</sup> and Kiessling.<sup>10</sup> A phase diagram for the Ta-B system given by Emrich<sup>11</sup> is from the work of Samsonov et al.<sup>12</sup>

In the present work, only the  $TaB_2$  compound will be considered since it is the most refractory and most thoroughly characterized compound in the Ta-B system.

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#### 27.1.1 Tantalum Diboride ( $\text{TaB}_2(\text{s}, \ell)$ )

##### a Crystal Structure and Melting Point

Tantalum diboride has a wide homogeneity range according to Kiessling<sup>1</sup> and Brewer et al.<sup>2</sup> It has an hexagonal structure of the  $\text{AlB}_2$  (C32) type.

A melting point of  $3200^\circ\text{C}$  ( $3473^\circ\text{K}$ ) has been reported by Post, Glaser, and Moskowitz.<sup>3</sup> Kieffer et al<sup>4</sup> have indicated that the melting point is greater than  $3000^\circ\text{C}$  ( $3273^\circ\text{K}$ ). Emrich<sup>5</sup> has reviewed the melting-point data and has found that reported values were in the range  $3000^\circ$  to  $3200^\circ\text{C}$ . He refers to a value  $3200^\circ\text{C}$  of Halden et al<sup>6</sup> and  $3100^\circ\text{C}$  by Samsonov and Portnoy.<sup>7</sup> In the present work, the intermediate value of  $3100^\circ\text{C}$  ( $3373^\circ\text{K}$ ) has been accepted.

Other works with data on  $\text{TaB}_2$  include the reviews by Samsonov and Markovskii,<sup>8</sup> and Aronsson.<sup>9, 7</sup>

##### b. Thermodynamic Properties

###### 1) Low-temperature heat capacity

When this analysis was initiated, no experimental data were

available. Mezaki et al<sup>11</sup> estimated via the Latimer method that  $S_{298.15}^{\circ}, \text{TaB}_2 = 11.3 \text{ e.u.}$  Emrich<sup>5</sup> tabulated a value of  $S_{298.15}^{\circ} = 13.9 \text{ e.u.}$  based on the work of Samsonov and Portnoy.<sup>7</sup> Kaufman<sup>12</sup> estimated that  $S_{298.15}^{\circ} = 9.90 \text{ e.u.}$  In the present work, Schick<sup>13</sup> used the Lindemann equation to estimate that

$$S_{298.15}^{\circ} = 10.603 \text{ e.u.}, \text{ and } H_{298.15}^{\circ} - H_0^{\circ} = 1.665 \text{ kcal gfw}^{-1}.$$

The latter entropy estimate and  $H_{298.15}^{\circ} - H_0^{\circ}$  value were accepted in the present work. These values were in good agreement with preliminary experimental data obtained by Westrum for a program at Man Labs directed by Kaufman and Clougherty.<sup>14</sup> The experimental data had yielded  $S_{298.15}^{\circ} = 10.57 \text{ e.u.}$  for  $\text{TaB}_{2.11}$ .

## 2) High-temperature heat content

Mezaki et al<sup>11</sup> reported high-temperature heat-content measurements for the range  $298.15^{\circ}$  to  $1126^{\circ}\text{K}$ . They found

$$C_{p, 298.15}^{\circ} = 13.98 \text{ cal deg K}^{-1} \text{ gfw}^{-1}, \text{ and}$$

$$C_{p, 1200^{\circ}\text{K}}^{\circ} = 21.89 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Mezaki<sup>15</sup> had apparently used the same data to derive a heat-capacity equation of the form

$$C_p^{\circ} = 11.38 + 8.76 \times 10^{-3} T \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

for the range  $298.15^{\circ}$  to  $1200^{\circ}\text{K}$ .

Enthalpy-content measurements were made by Neel et al<sup>16</sup> for the range  $502^{\circ}$  to  $4610^{\circ}\text{F}$  ( $534^{\circ}$  to  $2816^{\circ}\text{K}$ ) for a sample of tantalum boride later identified as  $\text{TaB}_2$ .<sup>17</sup> Further analysis of these data was given by Pears et al.<sup>18</sup>

In the present work, the original data of Neel et al<sup>16</sup> were converted to cgs units. A small correction of  $H_{298.15}^{\circ} - H_{273.15}^{\circ} = 280 \text{ cal/mole}$  was estimated. The results are shown on the following pages:

NEEL et al<sup>16</sup> DATA FOR TaB<sub>2</sub>

T °K	H <sup>°</sup> -H <sup>°</sup> <sub>T 298.15</sub> cal/mole
534.2	2893.9
544.8	3479.1
806.4	5820.2
813.1	6776.8
1100.9	12438.1
1370.3	18178.2
1614.2	24143.3
1918.7	29095.5
2144.2	38662.3
2547.0	42601.5
2816.4	52615.5

In the present work, to derive a high-temperature heat-capacity equation for TaB<sub>2</sub>, the Shomate method was used to treat both the Mezaki<sup>15</sup> and Neel et al<sup>16</sup> data. Using C<sub>p</sub><sup>°</sup>, 298.15 = 11.5 cal deg K<sup>-1</sup> gfw<sup>-1</sup>, the equation obtained is

$$C_p^{\circ} = 14.212 + 0.44947 \times 10^{-2} T - 0.36017 \times 10^6 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

The above equation, after integration, reproduces the experimental enthalpy contents to 12.0 percent or better. It has been found that the Mezaki data have always been larger than the calculated enthalpies,<sup>15</sup> whereas the Neel et al<sup>16</sup> data show positive and negative variations.

In the present work, the derived heat-capacity equation was extrapolated to the melting point. The heat of fusion for  $\text{TaB}_2$  was estimated to be  $20.0 \text{ kcal gfw}^{-1}$ , and the heat capacity for liquid  $\text{TaB}_2$  was estimated to be  $30.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

### 3) Heat of formation

Brewer and Haraldsen<sup>19</sup> had estimated the heat of formation of  $\text{TaB}_2$  to be more negative than  $-52 \text{ kcal/mole}$ . Samsonov<sup>20</sup> had estimated heats of formation of  $-63$  and  $-45.0 \text{ kcal/mole}$  by two different methods. Leitnaker<sup>21</sup> considered the heat-of-formation value to be in the range  $-126.0$  to  $-45.4 \text{ kcal/mole}$ . Leitnaker et al<sup>22</sup> considered the range to be  $-103.4$  to  $-45.4 \text{ kcal/mole}$ . Kaufman<sup>12</sup> estimated the heat of formation to be  $-57.4 \text{ kcal/mole}$ .

Referring to the above estimates and also by reference to the value accepted for  $\text{NbB}_2$  in the present work, it was estimated that  $\text{TaB}_2$  would have a heat of formation of about  $-50 \text{ kcal/mole}$ . This value would be subject to a considerable uncertainty, perhaps,  $\pm 15 \text{ kcal/mole}$ .

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## 27.2 Tantalum Carbides

### Phase Diagrams and General Information

Phase diagrams for the tantalum-carbon system have been presented by Hansen and Anderko<sup>1</sup> based on the work of Ellinger,<sup>2</sup> and more recently by Storms.<sup>3</sup> All of these works show the presence of only two compounds, Ta<sub>2</sub>C and TaC, both having variable ranges of composition. Accordingly, thermodynamic tables are prepared for these two phases of the stoichiometric composition.

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#### 27.2.1 Tantalum Carbide (TaC<sub>(s, l)</sub>)

##### a. Phase Data, Transition Points, and Melting Points

Tantalum carbide (TaC) exhibits a cubic (f. c. c.) structure of the NaCl (B1) type, according to Hansen and Anderko.<sup>1</sup> The lattice parameter is indicated to be 4.45 Å. This phase has a range of homogeneity of 40 to 49.7 atom-percent carbon (TaC<sub>0.67</sub> to TaC<sub>0.988</sub>), based on the observations of McMullin and Norton.<sup>2</sup> Storms<sup>3</sup> has reviewed more recent data. Bowman<sup>4</sup> found the range of homogeneity at 2400°C to be given by TaC<sub>0.71</sub> to TaC<sub>0.99</sub>. Robins<sup>5</sup> earlier found the upper limit to be TaC<sub>0.96</sub> but Storms<sup>3</sup> feels this is in error, and that the upper limit of TaC<sub>0.99</sub> is preferred.

Several authors have studied the variation of lattice parameter versus composition. Cooper and Hausler<sup>6</sup> found that for TaC<sub>0.861</sub> to TaC<sub>0.978</sub> the lattice parameter varied from 4.4353 to 4.4536 Å. Additional related work has been given Kempter and Nadler,<sup>7</sup> Brownlee,<sup>8</sup> Zalabak,<sup>9</sup> Bowman,<sup>4</sup> Robins,<sup>5</sup> and Smirnova and Ormont.<sup>10</sup> Smirnova and Ormont<sup>10</sup> studied the homogeneity limits TaC<sub>0.58</sub> to TaC<sub>0.91</sub> but indicate that the upper limit may possibly be TaC<sub>1.0</sub>.

Hansen and Anderko<sup>1</sup> do not indicate that any transitions occur in the TaC phase. Storms<sup>3</sup> is in agreement with this observation, the only transition discussed being the superconductive ones observed by

Giorgi *et al*<sup>11</sup> in the range 2.04 to 9.7°K. Recently, Shaffer<sup>12</sup> has found some evidence for different high temperature crystalline modifications of TaC. However, the evidence is very preliminary. Therefore, in the present work, we adopt the viewpoint that TaC retains its cubic structure with no phase transitions.

Melting points of 3730 to 3830°C were reported by Friederich and Sittig,<sup>13</sup> 3880 ± 150°C by Agte and Alterthum,<sup>14</sup> 3540°C by Geach and Jones,<sup>15</sup> and 3800°C by Ellinger.<sup>16</sup> Zalabak<sup>9</sup> also melted TaC and found values in the range 6360 to 6790°F (3788 to 4027°K). Storms<sup>3</sup> has drawn a tentative phase diagram for the TaC system and by analogy to the Nb-C system estimates that melting of TaC<sub>0.85</sub> occurs at 4000°C. His diagram for the TaC phase extends to TaC<sub>0.99</sub>. Eutectic melting at 3710°C is shown for the TaC<sub>1.0</sub> composition.

In view of the uncertainties of the melting point data, we have chosen the value 4000°C (4273°K) as shown by Storms for TaC<sub>0.85</sub> and applied it to the TaC<sub>1.0</sub> composition. Actually, of course, from Storms' tentative diagram, melting would occur over the range 3710 to 3820°C. Because of the uncertainties, however, the present approximation is utilized.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

Low-temperature heat capacity data for TaC was obtained by Kelley<sup>17</sup> for the range 54.6 to 294.5°K. Kelley and King<sup>18</sup> tabulate  $S_{298.15}^{\circ} = 10.11 \pm 0.08$  eu, and  $C_p^{\circ}(298.15) = 8.79$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>. In neither of these works have values of  $H_{298.15}^{\circ} - H_0^{\circ}$  been evaluated. In the present work, the original extrapolation to 0°K used by Kelley<sup>17</sup> for  $C_p^{\circ} = D \left( \frac{268}{T} \right) + E \left( \frac{861}{T} \right)$  has been used to evaluate  $H_{54.6}^{\circ} - H_0^{\circ} = 40.0$  cal gfw<sup>-1</sup>. Integration of the Kelley<sup>17</sup> data to 298.15°K, using the Kelley and King<sup>18</sup> value for  $C_p^{\circ}(298.15)$ , then gives  $H_{298.15}^{\circ} - H_0^{\circ} = 1.557$  kcal gfw<sup>-1</sup>.

For the present work, we accept the Kelley and King<sup>18</sup> value of  $S_{298.15}^{\circ} = 10.11$  eu, and our presently evaluated value of  $H_{298.15}^{\circ} - H_0^{\circ} = 1.557$  kcal gfw<sup>-1</sup>.

### 2) High-temperature heat capacity

Kelley,<sup>19</sup> in his 1960 tabulation, does not give any high-temperature heat capacity data for TaC. Neel, Pears, and Oglesby<sup>20</sup> made heat-content measurements in the range 508 to



4510°F (537.5 to 2760.9°K ). Their data have been converted to cgs units. A correction of 215 cal gfw<sup>-1</sup> was subtracted from the data to refer it to 298.15 degrees rather than the temperature of 273.15°K used by Neel et al.<sup>20</sup> The correction was obtained by integration of the low-temperature data mentioned earlier. The resulting enthalpy data are tabulated below.

ENTHALPY DATA FOR TaC FROM NEEL  
et al<sup>20</sup> CONVERTED TO cgs UNITS

T (°K)	H <sub>T</sub> <sup>°</sup> -H <sub>298.15</sub> <sup>°</sup> (cal/gfw)
537.5	2014.7
812.0	5037.8
1086.4	8425.3
1368.7	12541.8
1619.8	17151.4
1844.2	19509.8
2208.1	27442.7
2572.0	30444.3
2760.9	34517.9

Additional enthalpy data have been obtained by Mezaki,<sup>21</sup> who found an equation of the form:

$$C_p^{\circ} = 8.69 + 5.20 \times 10^{-3} T \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

to represent data obtained in the range 476.4 to 1113.2°K.

In the present work, the enthalpy data of Neel et al<sup>20</sup> and Mezaki<sup>21</sup> have been combined by the Shomate method using  $C_{p298.15}^{\circ} = 8.79$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> from Kelley and King.<sup>18</sup> The equation obtained is

$$C_p^{\circ} = 10.347 + 0.0027131T - 2.1033 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

This equation yields enthalpy contents which are 5 to 7 percent lower than the Mezaki experimental values and fit most of the Neel et al<sup>20</sup> data to less than 10 percent with the exception of their lowest temperature point, which has an experimental heat content 17.2 percent lower than that calculated from the equation. Although the data thus show considerable scatter, it is felt that the "averaged" equation as given is probably the best choice. This equation is then extrapolated to the melting point.

The heat of fusion was estimated to be  $25.0 \text{ kcal gfw}^{-1}$ . Above the melting point, the heat capacity of liquid TaC was estimated to be  $16.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

### 3) Heat of formation

There have been several reported calorimetric determinations of the heat of formation of  $\text{TaC}_{1.00}$ . Huber et al<sup>22</sup> recently studied 10 compositions in the TaC phase region. From  $\text{TaC}_{0.724}$  to  $\text{TaC}_{0.998}$ , the heat of formation varied from  $-27.1 \pm 1.3 \text{ kcal/gfw}$  to  $-34.6 \pm 1.2 \text{ kcal/gfw}$ . A linear extrapolation then yielded  $\Delta H_{f298.15}^{\circ}, \text{TaC}_{1.00} = -34.6 \pm 0.9 \text{ kcal gfw}^{-1}$ . In these calculations they assumed that the heat of formation of  $\text{Ta}_2\text{O}_5$  is  $-488.7 \pm 0.4 \text{ kcal gfw}^{-1}$ .

Kornilov, Leonidov, and Skuratov<sup>23</sup> found a heat of formation of  $-34.3 \pm 1 \text{ kcal gfw}^{-1}$  for the  $\text{TaC}_{1.00}$  composition, assuming that the heat of formation of  $\text{Ta}_2\text{O}_5$  is  $-489.3 \text{ kcal gfw}^{-1}$ . If the value of  $\text{Ta}_2\text{O}_5$  accepted on this project, i. e.,  $\Delta H_{f298.15}^{\circ} = -488.7 \text{ kcal gfw}^{-1}$  is used, then the new value based on the Kornilov et al<sup>23</sup> work becomes  $\Delta H_{f298.15}^{\circ}, \text{TaC} = -34.0 \text{ kcal gfw}^{-1}$ .

Humphrey<sup>24</sup> obtained a heat of formation of  $\Delta H_{f298.15}^{\circ}, \text{TaC} = -38.0 \text{ kcal gfw}^{-1}$ . Smirnova and Ormont<sup>10</sup> reported  $\Delta H_{f298.15}^{\circ}, \text{TaC} = -36 \text{ kcal gfw}^{-1}$  by using a heat of formation for  $\text{Ta}_2\text{O}_5$  of  $\Delta H_{f298.15}^{\circ} = -480.0 \text{ kcal gfw}^{-1}$ .

Using our presently accepted value, the heat of formation for TaC is converted to  $\Delta H_{f298.15}^{\circ}, \text{TaC} = -40.35 \text{ kcal gfw}^{-1}$ .

Huber et al<sup>22</sup> have reconciled the Humphrey<sup>24</sup> data by assuming that their sample may have contained free carbon. The Smirnova and Ormont<sup>10</sup> data were considered to be too erratic to be seriously considered.

In view of the above data, it appears that the recent Huber et al<sup>22</sup> data, which are in good agreement with the Kornilov et al<sup>23</sup> data, are to be preferred. Accordingly, we accept

$$\Delta H_{f298.15}^{\circ}, \text{TaC} = -34.6 \pm 0.9 \text{ kcal gfw}^{-1}.$$

### 4) Vaporization phenomena

By analogy with other refractory transition metal carbides, it is to be expected that TaC will vaporize directly to the elements. Langmuir vaporization experiments have been performed by Coffman et al<sup>25</sup> for the range 2267 to 3381 °K. Hoch et al<sup>26</sup> have also vaporized TaC.

In the present work, no analysis has been made of the vaporization data, since the calorimetric results are in such good agreement.

### Supplement

Additional high-temperature heat-content data have been reported by Levinson<sup>27</sup> for the range of 1296° to 2843°K. A preliminary look at the data suggests that the heat-capacity data from Levinson are somewhat lower than that obtained in the present tabulation. It was not possible to incorporate the Levinson data into the present tabulation because of time limitations.

A melting point of 3430°C for TaC has been reported by Engelke, Halden, and Farley.<sup>28</sup> This differs considerably from the value accepted in this work.

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## 27. 2. 2 Ditantalum Carbide ( $\text{Ta}_2\text{C}_{(s)}$ )

### a. Phase Data, Transition Points, and Peritectic Points

Hansen and Anderko<sup>1</sup> have presented a phase diagram prepared by Ellinger.<sup>2</sup> According to these works,  $\text{Ta}_2\text{C}$  has a variable range of homogeneity and undergoes a peritectic decomposition at  $\sim 3400^\circ\text{C}$  ( $3673^\circ\text{K}$ ).

$\text{Ta}_2\text{C}$  is hexagonal with  $a = 3.097 \text{ \AA}$  and  $c = 4.94 \text{ \AA}$ . Storms<sup>3</sup> indicates that the data of Lesser and Brauer<sup>4</sup> show that  $a = 3.101$  and  $c = 4.933 \text{ \AA}$  for  $\text{TaC}_{0.41}$  and  $a = 3.106$  and  $c = 4.945 \text{ \AA}$  for  $\text{TaC}_{0.50}$ . Storms<sup>3</sup> indicates that peritectic decompositions occur at  $3500^\circ\text{C}$ . At this temperature, the  $\text{Ta}_2\text{C}$  phase ( $\text{TaC}_{0.5}$ ) is in equilibrium with liquid  $\text{TaC}_{0.46}$  and solid  $\text{TaC}$  phase ( $\text{TaC}_{0.54}$ ). It should be noted that the data for the liquid phase are very approximate. In the present work, we accept the peritectic decomposition temperature presented by Storms, i. e.,  $3773^\circ\text{K}$ .

Hansen and Anderko<sup>1</sup> indicate that  $\text{Ta}_2\text{C}$  may exist as two modifications. There do not appear to be any definitive data to indicate the nature of these transitions, and we have ignored this possibility in preparing tables. Hence, we assume that the hexagonal structure is retained up to the peritectic point.

### b. Thermodynamic Properties

#### 1) Low-temperature heat capacity

No experimental low-temperature heat capacity data for  $\text{Ta}_2\text{C}$  have been reported. Krikorian<sup>5</sup> has estimated  $S_{298.15}^\circ = 20.8 \pm 1.0 \text{ e. u.}$  Smirnova and Ormont<sup>6</sup> have used the Eastman equation to estimate  $S_{298.15}^\circ = 19.86 \text{ eu.}$  Schick et al<sup>7</sup> have used Debye functions to estimate  $S_{298.15}^\circ = 18.133 \text{ eu.}$  Based on these estimates, we accept an intermediate value of  $19.5 \pm 1 \text{ eu.}$  Schicket al<sup>7</sup> also estimated  $H_{298.15}^\circ - H_0^\circ = 2.729 \text{ kcal gfw}^{-1}$ .

#### 2) High-temperature heat capacity

There have been no reported high-temperature heat capacity measurements for  $\text{Ta}_2\text{C}$ . For the present purpose, it appears most likely that an approximation by analogy to  $\text{Nb}_2\text{C}$  might be most satisfactory. Gel'd and Kusenko<sup>8</sup> found that

$$C_p^\circ = 15.88 + 3.0 \times 10^{-3} T - 2.050 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

The assumption was made that the heat capacity of  $\text{Ta}_2\text{C}$  at  $3000^\circ\text{K}$  would be  $1 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  larger than for  $\text{Nb}_2\text{C}$ . Hence, the

equation adopted becomes

$$C_p^\circ = 15.88 + 3.33 \times 10^{-3} T - 2.050 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

This equation is extrapolated to the peritectic temperature of 3773°K.

### 3) Heat of formation

A calorimetric heat of formation for Ta<sub>2</sub>C has been reported by Huber et al.<sup>9</sup> By linear extrapolation from the TaC<sub>0.485</sub> composition, they obtained  $\Delta H_{f298.15}^\circ, \text{Ta}_2\text{C} = -47.2 \pm 3.4 \text{ kcal gfw}^{-1}$ . In their calculations, they have used a heat of formation for Ta<sub>2</sub>O<sub>5</sub> of  $\Delta H_{f298.15}^\circ = -488.7 \text{ kcal gfw}^{-1}$  in agreement with the value selected in this compilation.

Earlier Smirnova and Ormont<sup>6</sup> found a value of  $\Delta H_{f298.15}^\circ, \text{Ta}_2\text{C} = -34.0 \text{ kcal gfw}^{-1}$  using a heat of formation of only  $-480.0 \text{ kcal gfw}^{-1}$  for Ta<sub>2</sub>O<sub>5</sub>. Correcting this, using the value  $-488.7 \text{ kcal gfw}^{-1}$  from the present tabulation, we obtain  $\Delta H_{f298.15}^\circ, \text{Ta}_2\text{C} = -42.7 \text{ kcal gfw}^{-1}$  for the heat of formation of Ta<sub>2</sub>C. This value is seen to be in moderate agreement with the Huber et al.<sup>1</sup> data. In the present case, we accept the Huber et al.<sup>1</sup> value, as their determination appeared to be more self-consistent than the work reported by Smirnova and Ormont.<sup>6</sup>

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### 27.3 Tantalum Nitrides

#### Phase Diagram and General Information

Hansen and Anderko<sup>1</sup> discuss the available phase data for the Ta-N system but do not give a phase diagram. The more recent work by Storms<sup>2</sup> reviews similar data but also does not show a phase diagram. Both works show that the Ta<sub>2</sub>N and TaN phases are the most important. Hansen and Anderko<sup>1</sup> note that Ta<sub>3</sub>N<sub>5</sub> and TaN<sub>2</sub> are unlikely. Osthagen and Kofstad<sup>3</sup> studied the reactions of tantalum and nitrogen in the range 800° to 1300°C. They reported the following phases to form: TaN<sub>0.05</sub>, Ta<sub>2</sub>N, TaN<sub>0.8-0.9</sub>, and TaN in general agreement with Schönberg.<sup>4</sup>

In the following work, the Ta<sub>2</sub>N and TaN phases are considered only. There are insufficient thermodynamic data to characterize the other possible phases.

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#### 27.3.1 Tantalum Nitride (TaN<sub>(s, l)</sub>)

##### a. Crystal Structure and Melting Point

According to Hansen and Anderko,<sup>1</sup> TaN has an hexagonal structure,  $a = 5.1911 \text{ \AA}$ ,  $c = 2.9107 \text{ \AA}$ , and  $c/a = 0.561$  based on the work of Brauer and Zapp.<sup>2</sup> Similar data had been reported by Schönberg<sup>3</sup> who found  $a = 5.185 \text{ \AA}$ ,  $c = 2.908 \text{ \AA}$ , and  $c/a = 0.561$ . Storms<sup>4</sup> also notes that Brauer and Zapp<sup>2</sup> had found the homogeneity range to vary from TaN<sub>0.98</sub> to TaN<sub>1.00</sub>. Storms points out that no cubic phase has been found for the TaN phase as was the case for the NbN

phase. Hence in the following work, it is assumed that TaN retains an hexagonal structure to its melting point.

There do not appear to have been any precise determinations of the melting point of TaN. It is believed that volatilization of nitrogen makes such measurements especially difficult. Friederich and Sittig<sup>5</sup> found 2890°C (3163°K), and Agte and Moers<sup>6</sup> found 3090°C (3363°K). In the present work, the latter value is adopted, but it is clear that it may have a large error.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

No experimental low-temperature heat-capacity data appear to be available for TaN. Kelley and King<sup>7</sup> do not list estimates or experimental data. Kubaschewski and Evans<sup>8</sup> have estimated the entropy  $S_{298.15}^{\circ} = 12.2 \pm 1.0$  e. u. Schick<sup>9</sup> estimated that  $C_p^{\circ} = 9.888$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>,  $S_{298.15}^{\circ} = 11.412$  e. u., and  $H_{298.15}^{\circ} - H_0^{\circ} = 1.779$  kcal gfw<sup>-1</sup>. For the present work, an intermediate, rounded value of entropy  $S_{298.15}^{\circ} = 12.0$  cal deg K<sup>-1</sup> gfw<sup>-1</sup> is used. The estimate of  $H_{298.15}^{\circ} - H_0^{\circ}$  is retained for use in the table preparation.

### 2) High-temperature heat content

Kelley<sup>10</sup> has tabulated the data of Sato<sup>11,12</sup> which give

$$C_p^{\circ} = 7.73 + 7.80 \times 10^{-3} T \text{ cal deg K}^{-1} \text{ gfw}^{-1}$$

for the range  $298.15^{\circ}\text{K} \leq T \leq 773^{\circ}\text{K}$ .

This equation leads to

$$C_p^{\circ}, 298.15 = 10.056 \text{ cal deg K}^{-1} \text{ gfw}^{-1},$$

in good agreement with the estimate noted in the previous section.

Data were reported by Pears et al<sup>13</sup> for a TaN phase. The material had a chemical analysis closer to that of Ta<sub>2</sub>N. Pears<sup>14</sup> has confirmed that their data pertain to the Ta<sub>2</sub>N phase. Hence, their data are not applicable to the TaN phase and are not considered here.

In the present work, the Kelley equation above has been accepted and extrapolated to 1000°K. At this temperature, the heat capacity is 15.53 cal deg K<sup>-1</sup> gfw<sup>-1</sup>. Above this temperature, the heat capacity is assumed constant with this same value.



At the melting point, the entropy of fusion is estimated to be  $5.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , leading to a heat of fusion of  $16,815 \text{ cal gfw}^{-1}$ . A truncated value of  $16,000 \text{ cal gfw}^{-1}$  is then accepted as the heat of fusion.

Above the melting point, the heat capacity was estimated to be  $15.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

### 3) Heat of formation

Neumann, Kröger, and Kunz<sup>15</sup> reported a heat of formation of TaN of  $-58.1 \text{ kcal gfw}^{-1}$ . They had used a heat of formation of  $\text{Ta}_2\text{O}_5$  of  $-499.9 \text{ kcal gfw}^{-1}$ , whereas the present work uses  $-488.7 \text{ kcal gfw}^{-1}$ . Their corrected heat of formation for TaN would then be  $-53.0 \text{ kcal gfw}^{-1}$ . Slade and Higson<sup>16</sup> obtained a heat of formation of  $-78.0 \text{ kcal gfw}^{-1}$  from dissociation-pressure measurements. Sato<sup>11</sup> used his heat-capacity data and the dissociation-pressure data of Andrews<sup>17</sup> to find that  $\Delta H_{f298.15}^\circ = -58.65 \text{ kcal gfw}^{-1}$ . Mah and Gellert<sup>18</sup> found by combustion calorimetry that the heat of formation is  $\Delta H_{f298.15}^\circ = 60.0 \pm 0.6 \text{ kcal gfw}^{-1}$ . Mah and Gellert used a heat of formation of  $-488.8 \text{ kcal gfw}^{-1}$  for  $\text{Ta}_2\text{O}_5$ . This is in good agreement with the presently accepted value of  $-488.7 \text{ kcal gfw}^{-1}$ . The corrected value for the heat of formation of TaN is then  $-59.95 \text{ kcal gfw}^{-1}$ . This value is accepted as the heat of formation for TaN as it agrees with the Sato<sup>11</sup> value and is in moderate agreement with the corrected value of Neumann et al.<sup>15</sup>

### 4) Vaporization

Andrews,<sup>17</sup> and Slade and Higson,<sup>16</sup> have studied vaporization from the TaN system. The reaction was considered to be  $2 \text{ TaN} \rightarrow 2 \text{ Ta} + \text{N}_2$  by Sato,<sup>11</sup> but it would appear that  $\text{Ta}_2\text{N}$  would form in preference to Ta. Bolgar, Verkhoglyadova, and Samsonov<sup>19</sup> studied vaporization of  $\text{Ta}_2\text{N}$  but obtained unreasonably low heats of vaporization. Gebhardt, Saghezzi, and Fromm,<sup>20</sup> and Pemsler,<sup>21</sup> also studied dissociation equilibria in the metal-rich region of the Ta-N system.

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### 27.3.2 Ditantalum Nitride ( $\text{Ta}_2\text{N}(\text{s}, \ell)$ )

#### a. Crystal Structure and Melting Point

According to Hansen and Anderko,<sup>1</sup>  $\text{Ta}_2\text{N}$  is hexagonal. Brauer and Zapp<sup>2</sup> found  $a = 3.048\text{\AA}$ ,  $c = 4.919\text{\AA}$ , and  $c/a = 1.61$ . The phase was homogeneous in the range  $\text{TaN}_{0.41}$  to  $\text{TaN}_{0.50}$ . Storms<sup>3</sup> has reviewed more recent data. Gebhardt *et al*<sup>4</sup> found that the homogeneity range is  $\text{TaN}_{0.36}$  to  $\text{TaN}_{0.5}$  at  $1000^\circ\text{C}$ , and  $\text{TaN}_{0.30}$  to  $\text{TaN}_{0.5}$  at  $2000^\circ\text{C}$ .

There do not appear to have been any experimental determinations of the melting point of  $\text{Ta}_2\text{N}$ . Based on the analogy to the Nb-N system and using the melting points of the elements as a guide, it would appear that a melting point of about  $3000^\circ\text{K}$  might be expected. Pears *et al*<sup>5</sup> heated samples of a sample originally quoted as TaN but later shown to be  $\text{Ta}_2\text{N}$  to  $2977^\circ\text{K}$  but did not report melting. Pemsler<sup>6,7</sup> made measurements of the  $\text{N}_2$  pressure over the Ta-N system. No definitive statement is made regarding the melting point for the  $\text{Ta}_2\text{N}$  composition, but it seems to be implied that the melting point does not change markedly from that of pure tantalum ( $3293^\circ\text{K}$ ).

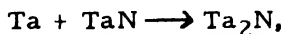
For the present work, the melting point for  $\text{Ta}_2\text{N}$  is assumed to be  $3000^\circ\text{K}$ , realizing it may be subject to an appreciable error.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at $298.15^\circ\text{K}$

In the absence of experimental data, it has been necessary to estimate low-temperature heat-capacity data for  $\text{Ta}_2\text{N}$ . Schick<sup>8</sup> estimated that  $C_{p,298.15}^\circ = 16.205 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ ,  $S_{298.15}^\circ = 21.245 \text{ e. u.}$ , and  $H_{298.15}^\circ - H_0^\circ = 3.163 \text{ kcal gfw}^{-1}$ .

For TaN, the entropy  $S_{298.15}^\circ$  had been estimated to be  $12.0 \text{ e. u.}$ . If the reaction below has  $\Delta S^\circ = 0$ ,



$$\begin{aligned} \text{then } S_{298.15}^\circ, \text{Ta}_2\text{N} &= S_{\text{TaN}}^\circ + S_{\text{Ta}}^\circ, \\ &= 12.0 + 9.92, \end{aligned}$$

$$S_{298.15}^\circ, \text{Ta}_2\text{N} = 21.92 \text{ e. u.}$$

For the present work, a rounded value of  $S_{298.15}^{\circ} = 22.0 \text{ e.u.}$ , is accepted. The other above estimates of  $C_p^{\circ}$  and  $H_{298.15}^{\circ} - H_0^{\circ}$  are retained.

## 2) High-temperature heat content

Pears et al<sup>5</sup> made heat-content measurements on a sample of tantalum nitride which they originally considered to be TaN. However, their chemical analysis and X-ray work showed that their material was actually Ta<sub>2</sub>N. Their data covered the range 588.7° to 2977.5°K. For the present purposes, it was necessary to convert their data to cgs units and to a room-temperature reference.\* The converted enthalpy data obtained are shown below.

### CONVERTED ENTHALPY-CONTENT DATA FROM PEARS et al FOR Ta<sub>2</sub>N

T	$H_T^{\circ} - H_{298.15}^{\circ}$
°K	cal gfw <sup>-1</sup>
588.7	6813.13
1034.81	15981.10
1366.48	21222.92
1616.48	26652.70
1905.37	32792.53
2188.70	42461.71
2505.37	52903.59
2755.37	60819.42
2949.81	56600.66
2977.59	62092.44

\*An estimated value of  $H_{298.15}^{\circ} - H_{273.15}^{\circ} = 350 \text{ cal gfw}^{-1}$  was used.

Referring to the foregoing data, one would not expect precise results (e. g., the value at 2949°K is less than that at 2755°K. However, the data were treated by the Shomate method, using  $C_p^\circ, 298.15 = 16.205 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ . The equation obtained is

$$C_p^\circ = 26.543 - 2.1104 \times 10^{-3}T - 0.86305 \times 10^{-6}T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

The above equation gave a maximum deviation of 13.3 percent at the lowest temperature. The equation leads to an unusual temperature dependence. It is felt that the equation is not very reliable. Because of the poor agreement obtained by this treatment, a more careful consideration of the Shomate plot of the Pears et al data was made. The Shomate function for the two lowest temperatures seemed to deviate considerably from the rest of the data. Accordingly, these two data points (588.7° and 1034.8°K) were discarded. The heat-capacity equation derived from the remaining higher-temperature points was then retained. The equation used follows:

$$C_p^\circ = 16.845 + 0.0042193T - 1.6868 \times 10^{-5}T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

The heat of fusion was estimated to be 22.0 kcal gfw<sup>-1</sup>, and the heat capacity of liquid Ta<sub>2</sub>N was estimated to be 22.5 cal degK<sup>-1</sup> gfw<sup>-1</sup>.

### 3) Heat of formation

Mah<sup>9</sup> found the heat of formation of Ta<sub>2</sub>N to be  $-64.7 \pm 3.0 \text{ kcal gfw}^{-1}$ . She used a sample containing 3.31 mole-percent Ta<sub>2</sub>O<sub>5</sub> and 5.34 mole-percent Ta in a bomb calorimeter. The purity is not especially good. Mah used a value of  $\Delta H_{f298.15}^\circ = -488.8 \text{ kcal gfw}^{-1}$  for Ta<sub>2</sub>O<sub>5</sub>. Using the value accepted in this work; i. e.,  $-488.7 \text{ kcal gfw}^{-1}$ , the heat of formation of Ta<sub>2</sub>N is revised to  $-64.6 \pm 3.0 \text{ kcal gfw}^{-1}$ .

Pemsler<sup>6, 7</sup> found that for the Ta<sub>2</sub>N composition  $\Delta H_{f3000}^\circ = -29.3 \text{ kcal g atom}^{-1}$  or  $\Delta H_{f3000}^\circ = -87.9 \text{ kcal gfw}^{-1}$ . Pemsler had made dissociation-pressure measurements. Since

$$\Delta H_{f3000}^\circ = \Delta H_{f298.15}^\circ + (H_T^\circ - H_{298}^\circ)_{\text{Ta}_2\text{N}} - 2(H_T^\circ - H_{298}^\circ)_{\text{Ta}} - 1/2 (H_T^\circ - H_{298}^\circ)_{\text{N}_2},$$

then

$$\begin{aligned}
\Delta H_{f298.15}^{\circ} &= \Delta H_{f3000}^{\circ} + 2(H_T^{\circ} - H_{298}^{\circ})_{Ta} + 1/2(H_T^{\circ} - H_{298}^{\circ})_{N_2} - (H_T^{\circ} - H_{298}^{\circ})_{Ta_2N}, \\
&= -87.9 + 2(19.982) + 1/2(22.160) - 59.705, \\
&= -87.9 + 39.964 + 11.080 - 59.705, \\
\Delta H_{f298.15}^{\circ} &= -96.561 \text{ kcal gfw}^{-1}.
\end{aligned}$$

Thus, it is seen that the Pemsler data differ considerably from the combustion data. Because of the high temperatures involved, the second-law dissociation-pressure data are probably not as precise as the combustion data. Therefore, the latter data are accepted.

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## 27.4 Tantalum Oxides

### Phase Diagrams and General Information

Hansen and Anderko<sup>1</sup> have summarized the work on the Ta-O system. They indicate that  $\text{Ta}_2\text{O}_5$  is the only solid compound definitely confirmed, although other compounds such as  $\text{Ta}_4\text{O}$ ,  $\text{Ta}_2\text{O}$ ,  $\text{TaO}$ ,  $\text{Ta}_2\text{O}_3$ , and  $\text{TaO}_2$  have been discussed in the literature.

Brauer, Müller, and Kühner,<sup>2</sup> by low-temperature oxidation of tantalum, reported the probable occurrence of  $\text{Ta}_6\text{O}$ . Earlier, Lagergren and Magneli<sup>3</sup> could not find any suboxide phases. Wasilewski<sup>4</sup> extended some earlier work<sup>5</sup> and found that samples thought to be  $\text{Ta}_2\text{O}$  were actually oxynitrides of the general formula  $\text{Ta}_2(\text{O}_x\text{N}_{1-x})$ . Wasilewski also annealed some Ta-O samples at  $1000^\circ\text{C}$  and found only Ta and  $\text{Ta}_2\text{O}_5$  phases. Wasilewski also noted a cubic phase which had only a transient existence. He postulates that this is a TaO phase which is probably metastable. He suggests this phase has 25 percent of its lattice sites unoccupied.

Further work which confirms the existence of only Ta and  $\text{Ta}_2\text{O}_5$  phases has been reported by Hoch and Mathur<sup>6</sup> who state that there are no intermediate oxides between Ta and  $\text{Ta}_2\text{O}_5$  in the range  $1450$  to  $1815^\circ\text{C}$ .

Thus it appears that  $\text{Ta}_2\text{O}_5$  is the only definite oxide to be considered. The suboxides such as  $\text{Ta}_6\text{O}$  reported by Brauer *et al.*,<sup>2</sup> and  $\text{TaO}_y$  and  $\text{TaO}_z$  by Norman,<sup>7</sup> and by Norman, Kofstad, and Krudtaa,<sup>8</sup> may exist over a limited temperature range or may be metastable structures. In any case, the necessary thermodynamic data for these phases are missing. In the present work, effort for condensed phases will be restricted to obtaining data for  $\text{Ta}_2\text{O}_5$ . For gaseous phases, both TaO and  $\text{TaO}_2$  will be considered.

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## 27. 4. 1 Tantalum Monoxide ( $\text{TaO}_{(g)}$ )

### a. Thermodynamic Functions

The first reported observation of bands due to TaO was reported by Kiess and Stowell.<sup>1</sup> They observed emission bands in the infrared, visible, and ultraviolet. However, no interpretation to yield spectroscopic constants was listed by Herzberg<sup>2</sup> or Rosen.<sup>3</sup> Fernando and Krishnamurty<sup>4</sup> have also observed the TaO bands.

Premaswarup<sup>5, 6</sup> has published rotational and vibrational analyses of the TaO bands which yielded  $r_e = 1.827 \text{ \AA}$  for the ground state. This value has been accepted in several analyses.<sup>7, 8</sup> However, Premaswarup and Barrow<sup>9</sup> have published a new analysis in which they state that the earlier work of Premaswarup<sup>5, 6</sup> was wrong.

In their work, Premaswarup and Barrow have obtained the data shown in table 58.

TABLE 58

DATA OBTAINED BY PREMASWARUP AND BARROW<sup>9</sup>

State	$\omega_e$ ( $\text{cm}^{-1}$ )	$x_e \omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$a_e$ ( $\text{cm}^{-1}$ )	$r_e$ ( $\text{\AA}$ )
$c^2\Delta$	903.01	4.15	0.3775	0.0019	1.743
$b^2\Pi$	$\left. \begin{array}{l} 898.5 \\ 896.0 \end{array} \right\}$	4.1	0.3772	0.0019	1.744
$a^2\Delta$	1031.7	5	0.4029	0.0020	1.687

A complete interpretation of the electronic states and their energy levels is not given. Thus, Premaswarup and Barrow<sup>9</sup> indicate that the coupling constant for the  $b^2\Pi$  state is  $\sim 1000 \text{ cm}^{-1}$  while that for an  $a^2\Delta$  is either about 300 or  $1700 \text{ cm}^{-1}$ , depending on whether the state is regular or inverted.

Barrow<sup>10</sup> has indicated that there are still many uncertainties regarding the TaO spectra. However, he prefers the regular rather than the inverted state. Thus, the following set of spectroscopic constants are accepted as shown in table 59.

TABLE 59  
DATA USED FOR TaO

State	g	$E$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e x_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$a_e$ ( $\text{cm}^{-1}$ )
c $^2\Lambda$	4	26679	903.01	4.15	0.3775	0.0019
b $\left\{ \begin{array}{l} ^2\Pi_{3/2} \\ ^2\Pi_{1/2} \end{array} \right.$	2	24364	898.5	4.1	0.3772	0.0019
	2	23348	896	4.1	0.3772	0.0019
a $\left\{ \begin{array}{l} ^2\Lambda_{5/2} \\ ^2\Lambda_{3/2} \end{array} \right.$	2	300	1031.7	5.0	0.4029	0.002
	2	0.0	1031.7	5.0	0.4029	0.002

In table 59, the value  $23348 \text{ cm}^{-1}$  was taken directly from Premaswarup and Barrow.<sup>9</sup> The value  $24364 \text{ cm}^{-1}$  was obtained as the sum of  $24064 + 300$ . The value  $24064 \text{ cm}^{-1}$  corresponds to the  $^2\Pi_{3/2} - ^2\Lambda_{5/2}$  transition from Premaswarup and Barrow.<sup>9</sup> The value for the energy level of the c state was taken from Premaswarup.<sup>5</sup> Splitting of this state was disregarded.

In the choice of data made, it is important to note that there are many uncertainties. Thus, Barrow<sup>10</sup> has pointed out that the a state has not been confirmed as the ground state. Furthermore, other low-lying states may be present which can affect the present calculations.

#### b. Heat of Formation

From the work of Inghram et al.,<sup>8</sup> data in the table 60 were analyzed. Free energy functions for Ta and  $\text{Ta}_2\text{O}_5$  were from the present project.

The heat of the sublimation reaction given in table 60 was found to be  $\Delta H_{s298.15}^\circ = 149.573 \text{ kcal/gfw}$ .

From Humphrey<sup>11</sup> the heat of formation of  $\text{Ta}_2\text{O}_5$  is  $\Delta H_{f298.15}^\circ = -488.800 \pm 0.500 \text{ kcal/mole}$ . Combining these data, it is found that

TABLE 60

VAPORIZATION OF  $\text{TaO(g)}$  VIA THE REACTION  $3/5 \text{ Ta}_{(s)} + 1/5 \text{ Ta}_2\text{O}_5(s) \rightarrow \text{TaO(g)}$

T (°K)	$P_{\text{TaO}}$ (atm)	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{Ta}}$ (cal deg K <sup>-1</sup> gfw <sup>-1</sup> )	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{Ta}_2\text{O}_5}$ (cal deg K <sup>-1</sup> gfw <sup>-1</sup> )	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{TaO}}$ (cal deg K <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_s^\circ$ 298.15 (kcal gfw <sup>-1</sup> )
2148	$1.35 \times 10^{-6}$	17.140	78.291	67.953	147.931
2275	$1.42 \times 10^{-5}$	17.481	81.251	68.387	145.214
2019	$2.74 \times 10^{-7}$	16.779	75.828	67.491	145.944
2176	$1.66 \times 10^{-6}$	17.217	78.904	68.051	148.812
2194	$1.82 \times 10^{-6}$	17.265	79.311	68.113	149.535
2170	$2.16 \times 10^{-6}$	17.200	78.770	68.030	147.300
2210	$4.6 \times 10^{-7}$	17.308	79.680	68.168	156.567
2309	$2.4 \times 10^{-6}$	17.570	82.102	68.499	155.285
average					149.573

$$\Delta H_f^\circ; \text{TaO}_{(g)}; 298.15 = 1/5 \left( \Delta H_f^\circ \text{Ta}_2\text{O}_5 \right) + \Delta H_s^\circ 298.15$$

$$= -97.6 + 149.573$$

$$\Delta H_f^\circ; \text{TaO}_{(g)}; 298.15 = +51.973 \text{ kcal/mole.}$$

This value of the heat of formation of  $\text{TaO}_{(g)}$  is accepted in the present tabulation. The uncertainty is expected to be  $\pm 5$  kcal/gfw.

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## 27. 4. 2 Tantalum Dioxide ( $\text{TaO}_2(\text{g})$ )

### a. Thermodynamic Functions

For the purpose of calculating thermodynamic functions for  $\text{TaO}_2(\text{g})$ , it has been necessary to make estimates of the spectroscopic constants. The calculations have then been made using the polyatomic gas computer program.

Brewer and Rosenblatt<sup>1</sup> calculated thermodynamic functions for  $\text{TaO}_2$  and other dioxides by assuming a linear configuration and using the valence bond theory. In the present work, a procedure similar to that of Brewer and Rosenblatt<sup>1</sup>, and as used for many other triatomic gases on this project, has been followed.

For the present work, it has been assumed that the vibrational frequency for the monoxide  $\text{TaO}$  is  $1031.7 \text{ cm}^{-1}$ . For this case, a stretching force constant of  $k_1 = 9.217 \times 10^5 \text{ dyne/cm}$  is calculated. The bending force constant was assumed to be  $0.0340 k_1$ . In this way, the valence bond theory yielded  $\omega_1 = 988.9 \text{ cm}^{-1}$   $\omega_2$  (doubly degenerate,  $= 279.7 \text{ cm}^{-1}$  and  $\omega_3 = 1072.8 \text{ cm}^{-1}$ .

The interatomic distance  $1.687 \text{ \AA}$  found for  $\text{TaO}$  was considered to be applicable to  $\text{TaO}_2$  also. Hence, a moment of inertia of  $15.12 \times 10^{-39} \text{ gm cm}^2$  or a rotational constant  $B_0 = 0.185111 \text{ cm}^{-1}$  was calculated.

To obtain the electronic contributions, it was desirable to use the ionic model as used by Brewer and Rosenblatt.<sup>1</sup> In the present case, however, Moore<sup>2</sup> does not tabulate data for the  $\text{Ta}^{+4}$  ion ( $\text{Ta V}$ ). However, Moore<sup>3, 4</sup> does tabulate data for  $\text{Nb}^{+4}$  and  $\text{V}^{+4}$ . Using these data as a guide, a crude estimate of the electronic energy levels was made as follows:

Degeneracy (Multiplicity)	Energy Level ( $\text{cm}^{-1}$ )
4	0
6	6000

### b. Heat of Formation

The vaporization data of Inghram et al<sup>5</sup> were analyzed by the third-law method according to the data shown in table 61.

TABLE 61

ANALYSIS OF DATA OF INGRAM et al<sup>5</sup> VIA THE REACTION  
 $1/5 \text{Ta}_{(s)} + 2/5 \text{Ta}_2\text{O}_{5(s)} \rightarrow \text{TaO}_{2(g)}$

T ° K	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{Ta}}$ cal degK <sup>-1</sup> gfw <sup>-1</sup>	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{Ta}_2\text{O}_5}$ cal degK <sup>-1</sup> gfw <sup>-1</sup>	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)_{\text{TaO}_{2(g)}}$ cal degK <sup>-1</sup> gfw <sup>-1</sup>	$\Delta H_{\text{reac}, 298}^\circ$ kcal gfw <sup>-1</sup>
2148	17.140	78.291	77.158	148.206
2019	16.779	75.828	76.402	143.197
2176	17.217	78.904	77.317	147.682
2206	17.298	79.588	77.486	150.224
2020	16.782	75.846	76.408	146.966
2170	17.200	78.770	77.283	146.042
2207	17.300	79.611	77.492	154.904
2314	17.583	82.221	78.081	152.953
Average				148.772

Using the average value for the heat of the above reaction in conjunction with the heat of formation accepted for  $\text{Ta}_2\text{O}_5$ , i. e.,  $\Delta H_{f298.15}^\circ = -488.7$  kcal gfw<sup>-1</sup>, it is found that the heat of formation of  $\text{TaO}_{2(g)}$  is given as

$$\begin{aligned}\Delta H_{f\text{TaO}_{2(g)}, 298.15}^\circ &= \Delta H_{\text{reac}, 298}^\circ + 2/5 \Delta H_{f\text{Ta}_2\text{O}_5}^\circ \\ &= 148.772 + 2/5 (-488.7)\end{aligned}$$

$$\Delta H_{f\text{TaO}_{2(g)}, 298.15}^\circ = -46.708 \text{ kcal gfw}^{-1}.$$

Ackerman and Thorn<sup>6</sup> have reviewed much of the other available data.

They have noted that the data of Goldstein et al<sup>7</sup> and Walsh and White<sup>8</sup> are in error because of loss of material from the effusion cell by diffusion through the container. Additional data on the reactions involving tantalum oxide gaseous species have been given by Goldstein et al<sup>9</sup> and Chupka et al.<sup>10</sup>

In the present work, the heat of formation derived from the Inghram<sup>5</sup> et al data is accepted. The value is considered subject to an uncertainty of  $\pm 10$  kcal gfw<sup>-1</sup>, as by Ackermann and Thorn. Thus, the heat of formation for TaO<sub>2</sub>(g) is  $\Delta H_{f298.15}^\circ = -46.708 \pm 10$  kcal gfw<sup>-1</sup>.

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### 27.4.3 Tantalum Pentoxide ( $\text{Ta}_2\text{O}_5(\text{s}, \ell)$ )

#### a. Phase Data, Transition and Melting Points

The data regarding structure and transition points for  $\text{Ta}_2\text{O}_5$  appear to be in dispute. Hansen and Anderko<sup>1</sup> indicate that only four X-ray investigations have been made by Lagergren and Magneli,<sup>2</sup> Wasilewski,<sup>3</sup> Schönberg<sup>4</sup> and Holser.<sup>5</sup> Holser<sup>5</sup> concluded that the so-called low-temperature ( $\beta$ ) form of  $\text{Ta}_2\text{O}_5$  has an orthorhombic structure which is isostructural with that of the low temperature form of  $\text{Nb}_2\text{O}_5$ .

Lagergren and Magneli<sup>2</sup> and Wasilewski<sup>3</sup> both observed a transition in  $\text{Ta}_2\text{O}_5$  at  $1320 \pm 20^\circ\text{C}$ . However, Schönberg<sup>4</sup> did not find such a transition. Furthermore, Kelley,<sup>6</sup> who has tabulated the best heat-content data of Orr<sup>7</sup> for the range 298 to  $1803^\circ\text{K}$ , does not indicate a transition point for  $\text{Ta}_2\text{O}_5$ . Hence, for the present work, we accept the viewpoint that there is no transition point. If later work shows such a transition, its heat of transition would probably be small, otherwise the Orr heat content data would have suggested such a transition.

Hansen and Anderko<sup>1</sup> do not list a melting point for  $\text{Ta}_2\text{O}_5$ . However, Kofstad<sup>8</sup> quotes a melting point of  $1470^\circ\text{C}$  ( $1743^\circ\text{K}$ ). Brewer<sup>9</sup> tabulates a melting point of  $2150 \pm 100^\circ\text{K}$  based on the work of Ruff, Siefert and Suda,<sup>10</sup> and Tiede and Birnbauer.<sup>11</sup> Kubaschewski and Evans<sup>12</sup> tabulate a value of  $1870^\circ\text{C}$  ( $2143^\circ\text{K}$ ). In the present work, we accept the Brewer value realizing it may be subject to change.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at $298.15^\circ\text{K}$

Kelley and King<sup>13</sup> tabulate the low-temperature results of Kelley.<sup>14</sup> The latter's measurements covered the range  $53.4$  to  $294.2^\circ\text{K}$ . Kelley<sup>14</sup> proposed the relation of Debye and Einstein functions given below to represent the heat capacity data below  $53.1^\circ\text{K}$ , namely

$$D\left(\frac{170}{T}\right) + 2E\left(\frac{265}{T}\right) + 2E\left(\frac{528}{T}\right) + 2E\left(\frac{880}{T}\right).$$

Kelley<sup>14</sup> found  $S_{298.15}^\circ = 34.2 \pm 0.4$  eu. Subsequently, Kelley and King<sup>13</sup> have tabulated  $S_{298.15}^\circ = 34.2 \pm 0.3$  eu. with  $C_p^\circ, 298.15 = 32.30$  cal deg  $\text{K}^{-1}$  gfw<sup>-1</sup>. Values of  $H_{298.15}^\circ - H_0^\circ$  were not obtained by the above workers. In the present work this quantity has



been evaluated.  $H_{53.4}^{\circ} - H_0^{\circ} = 106$  cal/mole and  $H_{298.15}^{\circ} - H_0^{\circ} = 5.495$  cal gfw<sup>-1</sup> were found. The entropy value of 34.2 eu at 298.15 °K from Kelley,<sup>14</sup> and Kelley and King<sup>13</sup> was used.

## 2) High-temperature heat content

The enthalpy content measurements of Orr<sup>7</sup> spanned the temperature interval 298.15 to 1803°K. Kelley<sup>6</sup> has indicated that their enthalpies were reproduced to 0.4 percent using an equation for  $C_p$  of the following form:

$$C_p^{\circ} = 37.0 + 6.56 \times 10^{-3} T - 5.92 \times 10^5 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

In the present work, this equation has been extrapolated to the melting point of 2150°K. A heat of fusion of 36.12 kcal gfw<sup>-1</sup> was estimated. The heat capacity of liquid Ta<sub>2</sub>O<sub>5</sub> was estimated to be 56 cal deg K<sup>-1</sup> gfw<sup>-1</sup>. These estimates were based on estimates by Kelley<sup>15</sup> and used by Inghram, Chupka and Berkowitz.<sup>16</sup>

## 3) Heat of formation

Humphrey<sup>17</sup> used oxygen bomb calorimetry to find that the heat of formation of Ta<sub>2</sub>O<sub>5</sub> is  $\Delta H_{f298.15}^{\circ} = -488.8 \pm 0.5$  kcal gfw<sup>-1</sup>. Kornilov, Leonidov, and Skuratov<sup>18</sup> found  $\Delta H_{f298.15}^{\circ} = -489.3 \pm 0.4$  kcal gfw<sup>-1</sup>. Huber *et al*<sup>19</sup> obtained  $\Delta H_{f298.15}^{\circ} = -487.7 \pm 0.9$  kcal gfw<sup>-1</sup>. Huber *et al*<sup>19</sup> have noted that Humphrey's value was based on an atomic weight of 180.88 rather than 180.95. The revised Humphrey value is thus  $-489.0 \pm 0.5$  kcal gfw<sup>-1</sup>. Huber *et al* have then adopted an averaged value of  $\Delta H_{f298.15}^{\circ} = -488.7 \pm 0.4$  kcal gfw<sup>-1</sup>. It is seen that this value agrees well (to within 0.6 kcal gfw<sup>-1</sup>) with the value of Kornilov *et al*. Accordingly, we accept the value  $\Delta H_{f298.15}^{\circ} = -488.7 \pm 0.4$  kcal gfw<sup>-1</sup> as the heat of formation of Ta<sub>2</sub>O<sub>5</sub>.

Earlier work by Smirnova and Ormont,<sup>20</sup> who also used bomb calorimetry, led to a heat of combustion for tantalum of only  $240.0 \pm 0.4$  kcal/g atom Ta, i. e.,  $\Delta H_{f298.15, \text{Ta}_2\text{O}_5}^{\circ} = -480.0 \pm 0.8$  kcal/gfw. It is likely that their experiments used impure Ta. Hence, their data are not considered here in view of the excellent agreement obtained by the other workers.

Additional work which shows the variation of O<sub>2</sub> partial pressure in the Ta-O system has been reported for limited ranges of composition. Thus, Kofstad<sup>8</sup> made studies in the Ta<sub>2</sub>O<sub>5</sub> homogeneity range. Pemsler<sup>21</sup> studied the solid solutions of tantalum containing up to 2.12 atom-percent oxygen. Brewer and Rosenblatt<sup>22</sup> have

indicated that  $O_2$  can be removed from tantalum by vacuum melting. The above work might be utilized to derive a free energy of formation of  $Ta_2O_5$  at an appropriate temperature by integrating the relative partial molar free energy contribution of oxygen,  $\overline{\Delta F}_{O_2}$  versus composition, but in view of the excellent agreement of the calorimetric data, this possibility was not considered necessary.

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## 28. Technetium Compounds

The only technetium compounds investigated in this study were the oxides.

### 28.1 Technetium Borides

The borides of technetium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 28.2 Technetium Carbides

The carbides of technetium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 28.3 Technetium Nitrides

The nitrides of technetium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 28.4 Technetium Oxides

In this study, detailed analyses of technetium oxides were made for  $\text{TcO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 28.4.1 Technetium Oxide (TcO<sub>(g)</sub>)

No spectroscopic data were available for gaseous TcO. The following values of  $\omega_e$  and  $r_e$  were estimated for this molecule.

$\omega_e$	$r_e$	$B_e$
cm <sup>-1</sup>	Å	cm <sup>-1</sup>
854	1.78 (1.77)	0.385

Values in parentheses were estimated by Brewer and Chandrasekharaiah.<sup>1</sup>  $B_e$  was calculated from the estimated  $r_e$  by the relation

$$B_e = \frac{1.686 \times 10^{-15}}{\mu r_e^2},$$

where  $B_e$  is in units of cm<sup>-1</sup>,  $\mu$  is the reduced mass in mass units, and  $r_e$ , the equilibrium internuclear distance, is in cm.

Thermodynamic functions for gaseous TcO have been calculated with the above constants; this is equivalent to assuming that the molecule is a rigid rotator and harmonic oscillator, and that there exists only a ground electronic state with a statistical weight of 4.

$D_0^\circ$  for TcO(g) was estimated to be 125 kcal/gfw from a comparison of adopted dissociation energies of monoxides of elements neighboring technetium in the periodic table. A  $\Delta H_{f298}^\circ$  for TcO(g) of 88.600 kcal/gfw was then calculated with appropriate thermodynamic functions from the present compilation. An uncertainty of  $\pm 15.000$  kcal/gfw was assigned to  $\Delta H_{f298}^\circ$ .

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## 29. Thorium Compounds

The only thorium compounds investigated in this study were the carbides and oxides.

### 29.1 Thorium Borides

The borides of thorium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 29.2 Thorium Carbides

In this study, detailed analyses of thorium carbides were made for  $\text{ThC}_{(s)}$ ,  $\text{ThC}_{2(s)}$ , and  $\text{ThC}_{2(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 29.2.1 Thorium Carbide ( $\text{ThC}_{(s)}$ , $\text{ThC}_{2(s)}$ , $\text{ThC}_{2(g)}$ )

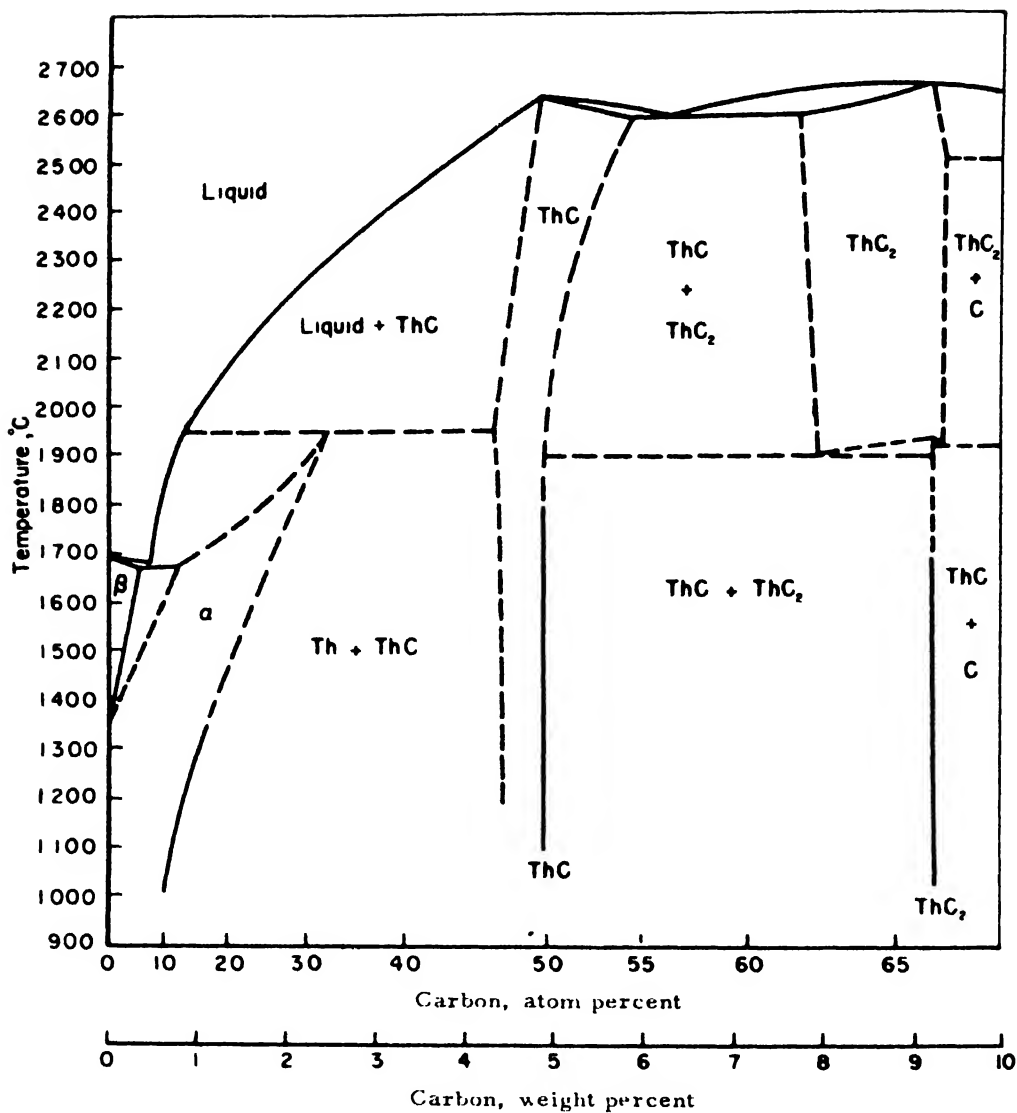
##### a. Phase Diagram, Crystal Structure, and Melting Point

A recent phase diagram (on next page) for the thorium-carbon system has been constructed by Rough and Chubb<sup>1</sup> on the basis of data by Wilhelm and Chiotti,<sup>2</sup> Wilhelm, Chiotti, Snow and Daane,<sup>3</sup> Brett, Law, and Livey<sup>4</sup> and Hansen and Anderko.<sup>5</sup> The melting points of  $\text{ThC}$  and  $\text{ThC}_2$  were found by Wilhelm and Chiotti<sup>2</sup> to be  $2989 \pm 25^\circ\text{K}$  and  $2928 \pm 25^\circ\text{K}$ , respectively, and these values have been accepted by Rough and Chubb.

The  $\text{ThC}$  phase has an f. c. c. ( $\text{NaCl}$  - type) structure with the lattice constant variously reported as 5.34 Å,<sup>1</sup> 5.325 Å,<sup>3</sup> and most recently 5.346 Å.<sup>6</sup> It appears that the variation in lattice parameter is a function of composition and that, therefore, there is a considerable degree of non-stoichiometry possible. Wilhelm, Chiotti, Snow, and Daane,<sup>3</sup> and Wilhelm and Chiotti<sup>2</sup> reviewed earlier work on  $\text{ThC}_2$  and reported the lattice to be pseudotetragonal. Hunt and Rundle,<sup>7</sup> using the results of neutron diffraction, and X-ray studies on single crystals, proposed the structure to be C-centered monoclinic with  $a_0 = 6.53$  Å,  $b_0 = 4.24$  Å, and  $c_0 = 6.56$  Å.

Recently, Kempter and Krikorian<sup>6</sup> have studied the X-ray powder patterns of  $\text{ThC}_2$  and report, on the basis of their interpretation of the analytical data, that the structure of  $\text{ThC}_2$  could be more conveniently interpreted as a pseudoorthorhombic lattice with parameters  $a_0 = 10.555$  Å,  $b = 8.233$  Å, and  $c = 4.201$  Å.

This is in agreement with the unpublished work of Baenziger reported by Wilhelm, Chiotti, Snow, and Daane.<sup>3</sup>



THORIUM - CARBON CONSTITUTIONAL DIAGRAM \*

\*Courtesy of F. Rough and W. Chubb, Battelle Memorial Institute.

## b. Thermodynamic Properties of the Condensed Phase

### 1) Heat-capacity data

For the present work, it was necessary to use estimated values for the entropy at 298.15°K since no experimental low-temperature data were available. We have accepted the entropy estimates of Krikorian,<sup>8</sup> who computed values of  $11.5 \pm 0.5$  eu. and  $15.1 \pm 3.0$  eu., respectively, for ThC and ThC<sub>2</sub>.

There are no experimental high-temperature heat capacity data for ThC and ThC<sub>2</sub>. We have used Krikorian's estimated values of  $S_{298}^{\circ}$ , and the three-parameter equation of the type suggested by Kelley<sup>9</sup> and presented by Krikorian,<sup>10</sup> to obtain the following heat-capacity relations:

$$C_p^{\circ}(\text{ThC}) = (12.43 \pm 0.30) + (1.87 \pm 0.04) \times 10^{-3}T \\ - (2.48 \pm 0.05) \times 10^5 T^{-2}.$$

$$C_p^{\circ}(\text{ThC}_2) = (12.60 \pm 1.16) + (2.00 \pm 0.18) \times 10^{-3}T \\ - (2.63 \pm 0.20) \times 10^5 T^{-2}$$

with  $C_p^{\circ}$  in units of cal/degK gfw.

The uncertainties in the  $C_p^{\circ}$  equation result from the uncertainty in  $S_{298}^{\circ}$ . These uncertainties have been used to compute the error tables for the condensed phases. It should be noted that any systematic error due to the use of these equations has not been included in the error tables.

### 2) Heats of formation

ThC: The only reported determination of the heat of formation of ThC is that of Huber and Holley<sup>11</sup> who measured the heat of combustion of ThC and deduced a value of  $\Delta H_{f298}^{\circ} = -7 \pm 6$  kcal/mole. The heat of formation had previously been estimated by Krikorian<sup>8</sup> as  $\Delta H_{f298}^{\circ} = -30 \pm 8$  kcal/mole from a consideration of this calculated value for ThC<sub>2</sub>. In this work we have selected the experimental value of Huber and Holley, with the reservation that we consider their value to be tentative.

ThC<sub>2</sub>: There do not appear to be any direct experimental measurements of the heat of formation of ThC<sub>2</sub>. The earliest attempt to determine this quantity was by Prescott and Hincke<sup>12</sup> who studied the reaction of ThO<sub>2</sub> with carbon. They obtained a heat of formation of ThC<sub>2</sub> of -78.9 kcal/mole. This value is incorrect because of errors in their thermodynamic data for ThO<sub>2</sub>, CO, and C. They found, however, for the reac-



tion  $\text{ThO}_2 + 4\text{C} \rightarrow \text{ThC}_2 + 2\text{CO}$  that  $\Delta F^\circ = 0$  (i. e., the equilibrium pressure was 1 atm) at 2395 °K. With this information, the third-law equation

$$\frac{\Delta H_{298}^\circ}{T} = \frac{\Delta F^\circ}{T} - \frac{\Delta(F_T^\circ - H_{298}^\circ)}{T},$$

and the free-energy functions listed below at 2395°K,

TABLE 62  
FREE-ENERGY FUNCTIONS FOR REACTION TO PRODUCE  $\text{ThC}_2$

Compound	$-(F_T^\circ - H_{298}^\circ)/T$ cal degK <sup>-1</sup> gfw <sup>-1</sup>	Reference
$\text{ThC}_2$	-31.055	Computed here
C	- 6.29	JANAF
$\text{ThO}_2$	-36.416	Computed here
CO	-56.296	JANAF

we obtain  $\Delta H_{298}^\circ = -197$  kcal/mole for the above reaction. From this, and the heats of formation of CO and  $\text{ThO}_2$  given by JANAF and Coughlin,<sup>13</sup> respectively, the heat of formation of  $\text{ThC}_2$  is found to be -43.4 kcal/mole.

An alternate method for the computation of the heat of formation of  $\text{ThC}_2$  is to use the vaporization data as described in paragraph(3) below. The latter computed value of  $\Delta H_{f298}^\circ = -46.6$  kcal/mole is accepted here, and was used to compute the last three columns of the  $\text{ThC}_2$  condensed phase table.

### 3) Vaporization data

The vaporization of  $\text{ThC}_2$  has been studied by Jackson, Barton, Krikorian, and Newbury<sup>14</sup> and by Lonsdale and Graves.<sup>15</sup> The study of Jackson et al involved the use of a mass spectrometer, and it was demonstrated that  $\text{ThC}_{(g)}$  does not exist, to a detectable extent, in the equilibrium vapor. The major vaporizing species was shown to be  $\text{ThC}_2$  with somewhat smaller amounts of Th present also. In the interpretation of their data, Lonsdale and Graves did not take  $\text{ThC}_2$  into consideration but assumed that the vaporization was by decomposition alone.

We are accepting the vaporization data of Jackson et al in this compilation. Their least-squares pressure curves for the pressures of  $\text{ThC}_2(\text{g})$  and  $\text{Th}(\text{g})$  over  $\text{ThC}_2(\text{s})$  are

$$\text{ThC}_2(\text{g}): \log P_{\text{atm}} = \frac{-39364 (\pm 163)}{T} + 7.20 (\pm 0.65),$$

$$\text{Th}(\text{g}): \log P_{\text{atm}} = \frac{-36025 (\pm 144)}{T} + 5.74 (\pm 0.57).$$

The pressure computed from the latter equation at 2500 °K has been used here to compute  $\Delta H_{298}^\circ = 184.3$  kcal/mole for  $\text{ThC}_2(\text{s}) \rightarrow \text{Th}(\text{g}) + 2\text{C}(\text{s})$ .

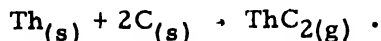
The third-law method was used in preference to the slope method for determining  $\Delta H_{298}^\circ$  because the latter is more sensitive to possible nonstoichiometry in the solid phase. There is serious disagreement between the second-law  $\Delta H_{298}^\circ$  ( $160.3 \pm 3.2$  kcal/mole) and that computed by the third law above.

The  $\Delta H_{298}^\circ$  value obtained above may be combined with the heat of vaporization of thorium previously tabulated to yield a heat of formation of 46.6 kcal/mole for  $\text{ThC}_2(\text{s})$ . This compares well with the value of 43.4 kcal/mole computed in paragraph (2) above.

The vapor pressure equation given above for



may be used as above to compute a third-law  $\Delta H_{298}^\circ = 209.8$  kcal/mole for the reaction. Again the third-law method is preferred over the second-law method which yields a  $\Delta H_{298}^\circ = 188$  kcal/mole. The accepted heat of sublimation may then be combined with the heat of formation of the solid to yield  $\Delta H_{f298}^\circ = 163.2$  kcal/mole for



The first five columns of the  $\text{ThC}_2$  gas table were computed from the  $\text{Th}(\text{g})$  table already tabulated in this work and from the Th-C and C-C distances estimated by Jackson et al (1.90 Å and 1.31 Å).<sup>14</sup> Similarly, Jackson's estimated vibration frequencies  $\omega_1 = 592$  cm<sup>-1</sup>,  $\omega_2 = 399$  cm<sup>-1</sup>, and  $\omega_3 = 1756$  cm<sup>-1</sup> were used. The electronic contribution was estimated by utilizing the first 10 energy levels reported for Th III.<sup>16</sup>

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### 29.3 Thorium Nitrides

The nitrides of thorium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 29.4 Thorium Oxides

In this study, detailed analyses of thorium oxides were made for  $\text{ThO}_{(g)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

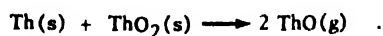
#### 29.4.1 Thorium Monoxide ( $\text{ThO}_{(g)}$ )

Calculations of the thermodynamic functions of gaseous thorium monoxide were based on the fragmentary spectroscopic data of Krishnamurty<sup>1</sup> and an estimated vibration frequency and internuclear distance. Krishnamurty reported lower electronic energy levels of 0, 2721, and 4177  $\text{cm}^{-1}$ , which he suggested were due to the splitting of a  $^3\pi$  ground state. This suggestion was adopted herein. The vibration frequency was estimated to be 800  $\text{cm}^{-1}$ , and the Th-O bond distance was taken to be 1.86 Å. No attempt was made to estimate the contribution of higher electronic energy levels. Spectroscopic constants derived from the above assumptions and used in the calculation of thermodynamic functions were (in units of  $\text{cm}^{-1}$ ) as follows:

State	E	$\omega_e$	$\omega_e x_e$	$B_e$	$a_e$	$D_e (\times 10^7)$
$\pi^3\pi$	$\left\{ \begin{array}{c} 0 \\ 2721 \\ 4177 \end{array} \right.$	800	3.5	0.327	0.0018	2.2

The vibration frequency had been estimated by Krishnamurty<sup>1</sup> to be 740  $\text{cm}^{-1}$ . The internuclear distance was estimated by Darnell, McCollum, and Milne<sup>2</sup> to be  $1.93 \pm 0.04$  Å from that frequency and Badger's rule. By using these last two quantities and Brewer and Chandrasekharaiah's<sup>3</sup> method of estimating the electronic partition function from the energy states of the + 2 ion, Darnell, McCollum, and Milne<sup>2</sup> calculated the entropy of  $\text{ThO}_{(g)}$  at 1883°K to be 79.3 e.u. This entropy was about 3.8 e.u. higher than the entropy at this temperature calculated herein.

In the course of studies on the vapor pressure of thorium metal, Darnell, McCollum, and Milne<sup>2</sup> made vaporization-rate measurements on the metal containing  $\text{ThO}_2$ . The high rates of vaporization in such a system was explained by the formation of  $\text{ThO}_{(g)}$  via the reaction



(IVB29.4.1-1)

From their assumption that the vaporization rates observed were for a system in equilibrium and that the activities of  $\text{ThO}_2(\text{s})$  and  $\text{Th}(\text{s})$  were unity, the standard heat of formation of  $\text{ThO}(\text{g})$  at 298.15 °K was recalculated with the thermodynamic functions for the metal and  $\text{ThO}(\text{g})$  given herein, thermodynamic functions for  $\text{ThO}_2(\text{s})$  from Kelley,<sup>4</sup> and the heat of formation of  $\text{ThO}_2(\text{s})$  from Huber, Holley, and Meierkord.<sup>5</sup> The value obtained for  $\text{ThO}(\text{g})$ ,  $\Delta H_{f298}^\circ$  was -7.640 kcal/gfw. This heat of formation would correspond to a dissociation energy at 0 °K of 204 kcal/gfw. The dissociation energy of  $\text{ThO}(\text{g})$  had been estimated by Brewer<sup>6</sup> to be  $200 \pm 20$  kcal/gfw.

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## 30. Titanium Compounds

Selected borides, carbides, nitrides, and oxides of titanium were investigated.

### 30.1 Titanium Borides

In this study, detailed analyses of titanium borides were made for  $\text{TiB}_2(\text{s}, \ell)$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 30.1.1 Titanium Diboride ( $\text{TiB}_2(\text{s}, \ell)$ )

##### a. Phase Diagrams, Crystal Structure, and Melting Point

At the present time, there does not appear to exist a completely definitive phase diagram for the titanium boron system. Hansen and Anderko<sup>1</sup> and Cisar<sup>2</sup> have published a diagram based on the work of Palty, Margolin, and Nielsen.<sup>3</sup> Their work covered the composition range 2- to 33-weight-percent boron in the titanium-boron system. According to their phase diagram, compounds of  $\text{Ti}_2\text{B}$ ,  $\text{TiB}$ ,  $\text{TiB}_2$ , and  $\text{Ti}_2\text{B}_5$  are possible. A further compound  $\text{TiB}_{12}$  has been discussed by Pearson.<sup>4</sup> Greenhouse, Accountius, and Sisler<sup>5</sup> found a high boron compound  $\text{TiB}_x$  but could not confirm it as being  $\text{TiB}_{12}$ .

More recently, Wittman, Nowotny, and Boller,<sup>6</sup> and Nowotny<sup>7</sup> have studied the binary Ti-B system. Their work showed evidence for only the  $\text{TiB}$  and  $\text{TiB}_2$  phases. No evidence could be found for  $\text{Ti}_2\text{B}$ ,  $\text{Ti}_2\text{B}_5$ , or higher compounds such as  $\text{TiB}_{12}$ . An explanation for the  $\text{Ti}_2\text{B}$  X-ray lines has been offered from the work of Aronsson,<sup>8</sup> which suggests that these lines are attributable to  $\text{TiB}$  reflections. Aronsson further doubts the existence of a binary cubic  $\text{TiB}$  phase and suggests that the observed "cubic  $\text{TiB}$ " phase is actually a ternary Ti-B-x phase. Other work for the ternary Ti-B-C and Ti-B-N systems have been given by Nowotny et al.<sup>9</sup>

From the available data, there is agreement that at least the  $\text{TiB}_2$  phase does exist; the other phase most likely to be confirmed is the  $\text{TiB}$  phase. The  $\text{TiB}_2$  phase, because of its more refractory nature relative to the other, disputed phases, has proven of most interest for contemporary studies and hence it will be studied first.

According to Norton, Blumenthal, and Sindeband,<sup>10</sup> the diborides  $\text{TiB}_2$ ,  $\text{ZrB}_2$ ,  $\text{NbB}_2$ ,  $\text{TaB}_2$ , and  $\text{VB}_2$  are isomorphous having a hexagonal C32-type structure. Thus, the structure is similar to that of  $\text{AlB}_2$  for this entire group of diborides. The structure given corresponds to alternate layers of metal and boron atoms. Recently, Johnson and Daane<sup>11</sup> have referred to work of Lipscomb and Britton<sup>12</sup> and Silver and Bray,<sup>13</sup> which suggests that in diborides the boron layers are isoelectronic with graphite.

For  $\text{TiB}_2$  Norton et al<sup>10</sup> found that  $a = 3.028\text{\AA}$ ,  $c = 3.228\text{\AA}$ , and  $c/a = 1.064$ . They also reported a density of  $4.52\text{ gm/cm}^3$ . Earlier, Ehrlich<sup>14</sup> had found  $a = 3.02\text{\AA}$ ,  $c = 3.21\text{\AA}$ , and  $c/a = 1.06$ . Brewer et al<sup>15</sup> found  $a = 3.028 \pm 0.003\text{\AA}$  and  $c = 3.230 \pm 0.003\text{\AA}$ . Because the lattice constants did not vary with composition, they concluded that the homogeneity range is narrow for  $\text{TiB}_2$ . Meerson and Samsonov<sup>16</sup> found that  $a = 3.020\text{ kX}$ ,  $c = 3.217\text{ kX}$ , and  $c/a = 1.065$ . They found a density of  $4.44\text{ gm/cm}^3$  via a pycnometric method.

The nature of the bonding in  $\text{TiB}_2$  is not well understood. Brewer and Haraldsen<sup>17</sup> and Samsonov<sup>18</sup> have discussed the importance of d-orbitals in the bonding in a qualitative sense. Aronsson<sup>8</sup> has briefly reviewed many of the concepts proposed. He tends to disagree with the concept that the borides are interstitial phases in the normal definition. Additional discussions of the borides may be found in Schwarzkopf and Kieffer.<sup>19</sup> Hume-Rothery and Raynor<sup>20</sup> point out the necessity for considering factors in addition to size factors. They point out the necessity of considering metal-nonmetal interactions. Flodmark<sup>21</sup> has made a quantum mechanical study of the borides, and his work illustrates the difficulties of obtaining quantitative theoretical data.

At the present time, it is clear that the nature of the bonding in borides, in general, is not understood. As Aronsson<sup>8</sup> has stated, it appears more evident now, than earlier, that the interactions between metal and nonmetal are of great importance to account for the high stability of these materials.

Melting points of  $2790^\circ\text{C}$  ( $3063^\circ\text{K}$ ) by Glaser,<sup>22</sup>  $2920^\circ\text{C}$  ( $3193^\circ\text{K}$ ) by Post et al,<sup>23</sup> and  $3203 \pm 60^\circ\text{K}$  by Samsonov and Petrash<sup>24</sup> have been reported. For the present compilation, the data of Post et al have been accepted.

## b. Thermodynamic Properties

### 1) Entropy and heat content at $298.15^\circ\text{K}$

No experimental low-temperature heat-capacity data have been published for  $\text{TiB}_2$ . However, Westrum<sup>25</sup> has obtained data for the related compound  $\text{ZrB}_2$ . Estimates of the entropy at  $298.15^\circ\text{K}$  for  $\text{TiB}_2$  have been made by Krestovnikov and Vendrikh,<sup>26</sup> giving  $S_{298}^\circ = 7.52\text{ cal deg K}^{-1}\text{ gfw}^{-1}$ , by Mezaki et al,<sup>27</sup> giving  $S_{298.15}^\circ = 6.2\text{ cal deg K}^{-1}\text{ gfw}^{-1}$ , by Kaufman,<sup>28</sup> giving  $S_{298}^\circ = 5.01\text{ cal deg K}^{-1}\text{ gfw}^{-1}$ , and by JANAF,<sup>29</sup> giving  $S_{298}^\circ = 6.6 \pm 0.5\text{ cal deg K}^{-1}\text{ gfw}^{-1}$ .

In the present work, calculations patterned after the Krestovnikov and Vendrikh<sup>26</sup> procedure were used. Using melting points of 1950°, 2450°, and 3063°K, respectively, for Ti, B, and TiB<sub>2</sub> (the slightly different melting point for TiB<sub>2</sub> from that accepted earlier would make only minor differences in results), and with density data taken from Hansen and Anderko<sup>1</sup> and a Lindemann constant of 137.0 for Ti and B, a value of  $S_{298.15}^{\circ} = 7.516 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  was obtained, in good agreement with Krestovnikov and Vendrikh. Also  $H_{298}^{\circ} - H_0^{\circ} = 1381 \text{ cal/mole}$  was found. Similar calculations for ZrB<sub>2</sub> had yielded  $S_{298}^{\circ} = 9.38 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ , which was  $0.80 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  larger than the experimental value of  $8.58 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  found by Westrum.<sup>25</sup> If this correction of  $0.80 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  is applied to the present calculations, one obtains  $S_{298.15}^{\circ} = 7.516 - 0.80 = 6.716 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . Accordingly,  $S_{298.15}^{\circ} = 6.7 \pm 0.5 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  which is in good agreement with other estimated values is accepted.

## 2) High-temperature heat content

Heat-capacity data at high temperatures for TiB<sub>2</sub> have been obtained by several investigators in recent years. Kelley<sup>30</sup> has tabulated an equation of the form,

$$C_p^{\circ} = 14.99 + 3.74 \cdot 10^{-3} T - 4.98 \cdot 10^{-5} T^{-1}, \quad (\text{IVB30.1.1-1})$$

for the range 298.15° to 1000°K based on the work of Walker, Ewing, and Miller<sup>31</sup> for the range 303° to 977°K. More recently, Mezaki et al<sup>27</sup> have performed drop calorimetry for the temperature range 420.4° to 1180°K. They have also smoothed their experimental data. Data have been obtained by a rate-of-cooling method by Prophet<sup>32</sup> for the range 1300° to 2150°K. Some data were reported in an earlier report<sup>33</sup> for a relatively impure sample (92-percent TiB<sub>2</sub>) for the range 1733° to 2417°K but are not considered further here. Krestovnikov and Vendrikh<sup>26</sup> found  $C_p^{\circ} = 7.219 + 1.147 \cdot 10^{-2} T \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$  from measurements between 300° to 1000°K. Work for the range 533° to 2755°K has been reported by Southern Research Institute.<sup>34</sup>

In table 63, comparisons of data obtained from these separate sources for the TiB<sub>2</sub> heat capacity and enthalpy content are summarized. It is seen that the Kelley<sup>30</sup> equation is in good agreement with the other tabulated data. At 298.15°K, the Kelley equation leads to  $C_p^{\circ} = 10.503 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ , whereas the Mezaki et al<sup>27</sup> data give  $C_p^{\circ} = 13.02 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ . Here, it is believed that the Kelley data are more realistic, and that the Mezaki equation is too high. Thus, Westrum<sup>25</sup> found that  $C_p^{\circ}(\text{ZrB}_2, 298.15) = 11.53 \text{ cal}^{\circ}\text{K}^{-1} \text{ gfw}^{-1}$ , and it seems reasonable that  $C_p^{\circ}(\text{TiB}_2, 298.15)$  should



TABLE 63

COMPARISON OF THERMAL DATA FROM VARIOUS SOURCES FOR  $T_{1B_2}$ 

T	Kelley <sup>30</sup> and Walker et al. <sup>31</sup>		Mezaki et al. <sup>27</sup>		Prophet <sup>32</sup>		Southern <sup>34</sup> Res. Inst.	Krestovnikov and Vendrikh <sup>26</sup>
	$C_p^\circ$	$H_T^\circ - H_{298}^\circ$	$C_p^\circ$	$H_T^\circ - H_{298}^\circ$	$C_p^\circ$ (observed)	$C_p^\circ$ (smoothed)	$C_p^\circ$	$C_p^\circ$ (measured)
$^\circ K$	cal $^\circ K^{-1}$ gfw $^{-1}$	kcal gfw $^{-1}$	cal $^\circ K^{-1}$ gfw $^{-1}$	kcal gfw $^{-1}$	cal $^\circ K^{-1}$ gfw $^{-1}$	cal $^\circ K^{-1}$ gfw $^{-1}$	cal $^\circ K^{-1}$ gfw $^{-1}$	cal $^\circ K^{-1}$ gfw $^{-1}$
298.15	10.503	0.000	13.02	0.000				
500	14.868	2.653	14.47	2.776			15.92	10.66
1000	18.232	11.052	18.01	10.897			17.75	18.69
1100	18.692	12.899					18.21	
1200	19.132	14.790	19.43	14.641	19.10	20.05	18.63	
1300	19.557	16.725					19.12	
1500	20.379	20.719			20.86	20.89	20.09	
2000	22.345	31.403						
2100	22.731	33.657			24.28	22.75	22.46	
2200	23.115	35.949			22.57	23.09	22.95	
2500	24.260	43.056					23.43	
2700	25.020	47.984					24.89	
3000	26.155	55.660					25.86	
							27.20	

be less than this value. Furthermore, the estimation procedure for low-temperature heat-capacity data using Debye functions leads to an estimate of  $C_{p, 298.15, \text{TiB}_2} = 10.152 \text{ cal } ^\circ\text{K}^{-1} \text{ gfw}^{-1}$ . The Kelley value is also in good agreement with the experimental data of Krestovnikov and Vendrikh<sup>26</sup> at 298.15°K.

In view of its good representation of the available experimental data even when extrapolated to temperatures near the melting point, the Kelley equation has been accepted for the present work for the range 298.15° to 3193°K.

Above the melting point, an estimated value of  $C_p^\circ = 25.0 \text{ cal } ^\circ\text{K}^{-1} \text{ gfw}^{-1}$  was used.

At the melting point of 3193°K adopted herein, the heat of fusion had to be estimated. The value chosen was 22,032 cal/mole calculated from the assumption that 2.3 e.u. represents the effect of the fusion. The uncertainty is estimated to be  $\pm 5000$  cal/mole.

### 3) Heat of formation

Work aimed at obtaining the heat of formation for  $\text{TiB}_2$  appears to have been initiated by Brewer and Haraldsen's<sup>17</sup> paper of 1955. From a study of nitride equilibria, they found

$$\Delta F_{1820}^\circ \text{ } ^\circ\text{K, TiB}_2 \text{ formation} \sim -71.4 \text{ kcal/gfw.} \quad (\text{IVB30.1.1-2})$$

Using the assumption that  $\Delta S^\circ$  and  $\Delta C_p^\circ = 0$ , they derived

$$\Delta H_{f, 298.15, \text{TiB}_2}^\circ \sim -71 \text{ kcal/gfw.} \quad (\text{IVB30.1.1-3})$$

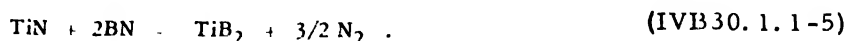
At about the same time, Samsonov<sup>35</sup> used a "tensimetric method" in the reduction of titanium oxide by carbon and boron carbide, to obtain

$$\Delta H_{f, 298.15, \text{TiB}_2}^\circ = -70.04 \text{ kcal/gfw.} \quad (\text{IVB30.1.1-4})$$

This method does not necessarily refer to equilibrium conditions since a rate of change of pressure is observed; chemical reactions and other rate processes may be occurring. Further questions have also been raised by the choice of auxiliary data used by Samsonov. Thus, Armstrong and Krieger<sup>36</sup> note that Samsonov and Markovski<sup>37</sup> have used a heat of formation value for  $\text{B}_4\text{C}$  equal to -66.0 kcal/mole, whereas the accepted western value is about -12.2 kcal/mole. Williams<sup>38</sup> has also reviewed these data, as

well as other data, and concludes that the Samsonov and Markovski value is not correct. He also questions the  $B_4C$  data used by Samsonov.<sup>35</sup>

Williams has performed nitride equilibria similar to the experiment of Brewer and Haraldsen.<sup>17</sup> Williams<sup>38</sup> has discussed the Brewer and Haraldsen<sup>17</sup> data as well as his own. His work yielded a transition temperature of  $2150^\circ \pm 25^\circ K$  for the reaction



This is considerably higher than the value  $1820^\circ K$  determined by Brewer and Haraldsen. Aside from this, Williams pointed out that a better choice of data for BN leads to a heat of formation of  $TiB_2$  of  $-84$  kcal/mole from the Brewer and Haraldsen data. From his own data, Williams reports  $\Delta F_{fTiB_2, 2150^\circ K}^\circ = -66$  kcal/mole. If this is converted to  $298.15^\circ K$  using the data herein for  $298.15^\circ K$  one would obtain

$$\Delta H_{f298, TiB_2}^\circ \approx -76 \text{ kcal/mole.} \quad (IVB30.1.1-6)$$

If the basic Williams<sup>38</sup> data are recomputed, one finds that

$$\Delta F_{2150^\circ K}^\circ = -RT \ln \frac{a_{N_2}^{3/2} a_{TiB_2}}{a_{TiN} a_{BN}^2} \quad (IVB30.1.1-7)$$

Assuming that activities of the solid phases are unity and that  $P_{N_2} = 0.5 \text{ atm}$  as reported by Williams, one obtains

$$\begin{aligned} \Delta F_{2150^\circ K}^\circ &= -4.575 \times 2150 \times 3/2 \log 0.5 \\ &= -4.575 \times 2150 \times 1.5 \times (-0.30103) \quad (IVB30.1.1-8) \\ &+ 4442.8 \text{ cal.} \end{aligned}$$

Then using data for BN and TiN from the JANAF tables,<sup>39</sup> one calculates

$$\Delta F_{2150^\circ K}^\circ = \Delta F_{fTiB_2}^\circ - \Delta F_{fTiN}^\circ - 2 \Delta F_{fBN}^\circ, \quad (IVB30.1.1-9)$$

or

$$\begin{aligned} \Delta F_{fTiB_2}^\circ &= \Delta F_{2150}^\circ + \Delta F_{fTiN}^\circ + 2 \Delta F_{fBN}^\circ \\ &= 4.443 + (-31.879) + 2(-15.397), \quad (IVB30.1.1-10) \end{aligned}$$

$$\Delta F_{\text{TiB}_2, 2150^\circ\text{K}}^\circ = -58.223 \text{ kcal/mole.} \quad (\text{IVB30. 1. 1-11})$$

Converting these data then gives

$$\Delta H_{f298, \text{TiB}_2}^\circ = -70.26 \text{ kcal/mole.} \quad (\text{IVB30. 1. 1-12})$$

This final value of -70.26 kcal/mole as the heat of formation for  $\text{TiB}_2$  via nitride equilibrium is believed more realistic than the value -76 kcal gfw<sup>-1</sup> which is based on Williams' own calculation, or the value  $-73.6 \pm 4.0$  kcal gfw<sup>-1</sup> as recalculated by JANAF.<sup>29</sup> It is possible that both Williams<sup>38</sup> and JANAF<sup>29</sup> may have neglected the contribution due to  $\text{N}_2$  pressure being less than atmospheric.

A direct reaction calorimeter at high temperatures was used by Lowell and Williams<sup>40</sup> to give  $\Delta H_{f298, \text{TiB}_2}^\circ = -50 \pm 5$  kcal/mole. They also found that  $\Delta H_{f\text{TiC}}^\circ = -45.5 \pm 4.6$  kcal/mole and that  $\Delta H_{f\text{SiC}}^\circ = -12.0 \pm 4.0$  kcal/mole. It should be pointed out that these auxiliary data do not necessarily prove that their method is exact. Although the TiC data are in general agreement with several determinations by Humphrey,<sup>41</sup> Chupka et al,<sup>42</sup> and Coffman et al,<sup>43</sup> there are other recent data favoring a more negative heat of formation for TiC, such as the electrochemical determination of  $\Delta H_{f298, \text{TiC}}^\circ = -54.0$  kcal gfw<sup>-1</sup> by Smirnov and Krasnov<sup>44</sup> and the calorimetric value of  $-55.0 \pm 0.3$  kcal/gfw reported by Morozova, Khripun, and Ariya.<sup>45</sup>

In the case of the heat of formation of SiC, a great deal of evidence suggests its heat of formation is more negative. Recently, D'Entremont and Chipman<sup>46</sup> found that  $\Delta H_{f298, \text{SiC}}^\circ = -15.8$  kcal gfw<sup>-1</sup> via solubility in molten silver. Several other determinations by Humphrey et al,<sup>47</sup> Drowart and DeMaris,<sup>48</sup> Davis et al,<sup>49</sup> Grieveson and Alcock,<sup>50</sup> and Kay and Taylor<sup>51</sup> when recalculated using new data also give values in the range -15 to -20 kcal/gfw. These data for TiC and SiC are not intended as definitive values, but the indications are that, if anything, the Lowell and Williams<sup>40</sup> results should be more negative. If consistent errors are common in their determination, it would appear that the heat of formation of  $\text{TiB}_2$  should also be more negative. It is suggested that vaporization of a portion of their specimen; i.e., vaporization of elemental boron or titanium being an endothermic process, would thus not permit a sufficiently large release of energy when the elements are combined under the high-temperature conditions of their experiment. It would also be expected that the amount of error would be greater in the case of borides than carbides since elemental boron is significantly more volatile than carbon.

Oxygen-bomb calorimetry was used by Epel'baum and Starostina<sup>52</sup> to give  $\Delta H_{f298, \text{TiB}_2}^\circ = -66.85 \pm 2.7 \text{ kcal/gfw}$ . Armstrong and Krieger<sup>36</sup> have commented on the fact that their heat-of-combustion value for elemental boron is smaller than the accepted value. It is clear that this casts some doubts on their data; however, it is also noteworthy that their value for  $\text{ZrB}_2$  of  $\Delta H_f^\circ = -75.02 \pm 3.35$  is in good accord with recent determinations for  $\text{ZrB}_2$  by other investigators. In a review of the  $\text{ZrB}_2$  work discussed separately, a value of  $\Delta H_{f298}^\circ = -73 \text{ kcal gfw}^{-1}$  was accepted. Hence, if the work for  $\text{TiB}_2$  were carried out analogously to that for  $\text{ZrB}_2$  it would seem that the value of  $\text{TiB}_2$  was essentially correct or should be slightly changed with a positive correction to be consistent with the  $\text{ZrB}_2$  data. A suggested change of 2 or 3 kcal/gfw thus give  $\Delta H_{298, \text{TiB}_2}^\circ \approx -65 \text{ kcal/gfw}$ .

Vaporization studies for  $\text{TiB}_2$  have been reported by several investigators. Schissel and Williams<sup>53</sup> had obtained a heat of formation of  $\Delta H_{f298, \text{TiB}_2}^\circ = -32 \text{ kcal/gfw}$ , but more recent work shows this to be in error.

Schissel and Trulson<sup>54</sup> from a mass spectrometric study derived  $\Delta H_{f298}^\circ = -52 \pm 6.0 \text{ kcal gfw}^{-1}$ . However, their data utilized free-energy functions for  $\text{TiB}_2$ , which were too large numerically, since they added the contributions from the separate elements. Their work considers  $\text{TiB}_2$  to vaporize congruently at the stoichiometric composition.

Bolgar, Verkhoglyadova, and Samsonov<sup>55</sup> have studied the rate of vaporization of  $\text{TiB}_2$  by a Langmuir technique. They found a slight composition change with vaporization. They concluded that the diboride vaporizes as molecular species with a heat of vaporization of only 45.70 kcal/gfw. These data are more realistic if treated by the Third-Law method; however, the data they have tabulated for a series of materials appeared to give too high volatilities and hence unrealistic heats of formation. It should also be pointed out that their conclusion regarding molecular species is contradicted by the work of Schissel and Williams,<sup>53</sup> and Schissel and Trulson,<sup>54</sup> who found only atomic species.

Resonance-line-absorption studies for the vaporization of  $\text{TiB}_2$  in the presence of  $\text{B}_4\text{C}$  have been reported by Kibler et al.<sup>56</sup> In their work, it was necessary to measure only the titanium partial pressure since that for boron was held constant. From their data, they derive, for the formation of  $\text{TiB}_2$  from  $\text{Ti}_{(\ell)}$  and  $\text{B}_{(\ell)}$  that

$$\Delta F_{f, 2475}^\circ = -53.34 \text{ kcal/gfw.} \quad (\text{IVB30.1.1-13})$$

Using free-energy functions for  $\text{TiB}_2$ ,  $\text{Ti}_{(\text{ref})}$ , and  $\text{B}_{(\text{ref})}$  from the present and earlier<sup>33</sup> tabulations, one obtains

$$\begin{aligned}\Delta H_{f298}^{\circ} &= \Delta F_{f,2475}^{\circ} + \frac{T}{1000} \left[ f_{\text{efTiB}_2} - f_{\text{efTi}_{(\text{ref})}} - 2 f_{\text{efB}_{(\text{ref})}} \right] \\ &= -53.340 + \frac{2475}{1000} [26.653 - 16.812 - 2(7.733)] \\ &= -53.340 + \frac{2475}{1000} [-5.625]\end{aligned}$$

$$= -67.261 \text{ kcal/gfw.} \quad (\text{IVB30.1.1-14})$$

If the free-energy functions which Stull<sup>1</sup> and Sinke<sup>57</sup> tabulate for elemental Ti and B had been used, and which Kibler et al<sup>56</sup> had used, one would find a slight difference because of the boron data since the Stull and Sinke value is about 0.262 unit smaller in absolute value than the presently tabulated Avco RAD values. Thus, one obtains

$$\Delta H_{f298}^{\circ} = -53.340 + \frac{2475}{1000} (-5.101)$$

$$= -53.340 - 12.625 = -65.964 \text{ kcal/gfw} \quad (\text{IVB30.1.1-15})$$

Schissel and Trulson<sup>54</sup> reported mass spectrometric vaporization of  $\text{TiB}_2$ . They studied vaporization for three cases; first,  $\text{TiB}_2$  plus excess boron; second,  $\text{TiB}_2$  alone; and third,  $\text{TiB}_2$  plus excess titanium. For the third case, they also obtained data for the disputed TiB phase. It is possible that the presence of carbon accounts for the phase as discussed earlier by Aronsson.<sup>8</sup> Their experiments covered the range 2063° to 2462°K and gave an average  $\Delta H_{298}$  430 kcal/mole. They assumed that the free-energy functions for  $\text{TiB}_2$  were equivalent to the sum of the free-energy functions for  $\text{Ti}_{(\text{ref})} + 2\text{B}_{(\text{ref})}$ . That is, they assumed  $\Delta C_p^{\circ}$  and  $\Delta S^{\circ}$  were zero. For the first case involving  $\text{TiB}_2$  plus excess boron, they accepted boron vapor-pressure data as tabulated by JANAF<sup>39</sup> to calculate the titanium partial pressure from their relation

$$P_{\text{Ti}} = P_{\text{B}} \frac{I_{\text{Ti}} T_{\text{Ti}} (\sigma_i S)_{\text{B}}}{I_{\text{B}} T_{\text{B}} (\sigma_i S)_{\text{Ti}}} \quad (\text{IVB30.1.1-16})$$

Analyzing their data, they obtained

$$\Delta H_{298, \text{TiB}_2}^{\circ} \text{ sub} = 431.4 \text{ kcal/mole}, \quad (\text{IVB30.1.1-17})$$

and

$$\Delta H_{f, \text{TiB}_2, 298.15}^{\circ} = -53.7 \pm 0.7 \text{ kcal/mole} . \quad (\text{IVB30.1.1-18})$$

For the second system of  $\text{TiB}_2$  + graphite, pressures of Ti and B were obtained somewhat differently by using a silver-calibration method often used in mass spectrometric work. For this case, they obtained

$$\Delta H_{298, \text{TiB}_2}^{\circ} \text{ sub} = 429.6 \text{ kcal/mole}, \quad (\text{IVB30.1.1-19})$$

and

$$\Delta H_{f, \text{TiB}_2, 298}^{\circ} = -51.9 \pm 1.1 \text{ kcal/gfw} \quad (\text{IVB30.1.1-20})$$

For the third system of  $\text{TiB}_2$  + Ti, pressure data were again obtained by the silver-calibration method. From the data for this system, Schissel and Trulson<sup>54</sup> found

$$\Delta H_{298, \text{TiB}_2}^{\circ} \text{ sub} = 428.6 \text{ kcal/mole}, \quad (\text{IVB30.1.1-21})$$

and

$$\Delta H_{f, \text{TiB}_2, 298}^{\circ} = -50.9 \pm 0.7 \text{ kcal/mole}. \quad (\text{IVB30.1.1-22})$$

Some Schissel and Trulson<sup>54</sup> data, using the presently available free-energy functions for  $\text{TiB}_2$  and using the functions for  $\text{Ti}_{(g)}$  and  $\text{B}_{(g)}$  from Barriault et al,<sup>33</sup> have been recomputed. It was found that, between 2244° and 2408°K, corrections of 11.3 and 12.4 kcal/mole, respectively, must be added to the heats of vaporization quoted by Schissel and Trulson. Thus, the average  $\Delta H_{298, \text{TiB}_2}^{\circ} \text{ sub}$  should be increased from 430 to about 441.5 kcal/mole.

Schissel and Trulson had also obtained a Second-Law value for the sublimation of  $\Delta H_{2287}^{\circ} = 424 \pm 14 \text{ kcal/mole}$ ; i.e.,

$$\begin{aligned} \Delta H_{298}^{\circ} &= \Delta H_{2287}^{\circ} + (H_T^{\circ} - H_{298}^{\circ})_{\text{TiB}_2} - (H_T^{\circ} - H_{298}^{\circ})_{\text{Ti}} - 2 (H_T^{\circ} - H_{298}^{\circ})_{\text{B}} \\ &= 424 + 37.976 - 10.812 - 2 \times 9.881 \\ &= 431.402 \pm 14 \text{ kcal/mole} . \end{aligned} \quad (\text{IVB30.1.1-23})$$

The agreement between Second- and Third-Law heats is within the limits of accuracy specified for the Second-Law measurement. However, it is believed that the Third-Law value is more correct because of the problems of accurately measuring temperature coefficients at the high temperatures involved.

Assuming that the sublimation of  $\text{TiB}_2$  can be represented by  $\Delta H_{298}^\circ = 441.5$  kcal/mole, it is possible to calculate the heat of formation. However, it is necessary to have, as auxiliary data, the heats of sublimation for  $\text{Ti}_{(g)}$  and  $\text{B}_{(g)}$ . It is also well to remember, from the discussions of elemental boron sublimation, that the heat of sublimation of boron is still not too accurately known. If one uses the data thus far available from the present and earlier reports<sup>33</sup> for  $\text{Ti}_{(g)}$  and  $\text{B}_{(g)}$  and the calorimetric heat of formation of Epel'baum and Starostina,<sup>52</sup> a heat of sublimation,

$$\Delta H_{298}^\circ = +66.85 + 112.49 + 2(133) \\ = 445.34 \text{ kcal/mole,} \quad (\text{IVB30.1.1-24})$$

is obtained. It is seen that these data give an agreement which is probably within the accuracy with which the heat of sublimation is known. From earlier discussions, it had been suggested that the calorimetric heat of formation for  $\text{TiB}_2$  might be reduced to  $\Delta H_{298}^\circ = -65$  kcal/mole. If the heat of sublimation for boron were also reduced to 132 kcal/mole, then one would obtain

$$\Delta H_{298, \text{sub}, \text{TiB}_2}^\circ = 65 + 112.49 + 2(132) \\ = 441.49 \text{ kcal/mole,} \quad (\text{IVB30.1.1-25})$$

which is in good agreement with the observed Third-Law heat.

In concluding this study of the heats of formation for  $\text{TiB}_2$ , it appears most prudent to use the calorimetric value of Epel'baum and Starostina;<sup>52</sup> i.e.,  $\Delta H_{298}^\circ = -66.85$  kcal/mole. The vaporization studies of Kibler et al<sup>56</sup> by a spectroscopic technique lead to  $\Delta H_{298}^\circ = -67.2$  or  $\Delta H_{298}^\circ = -65.9$  kcal/mole, depending on treatment of the data. These values are in good agreement with the calorimetric values. It should be pointed out that the vaporization studies of Kibler et al eliminated the problem of studying boron vapor pressure by holding this quantity fixed with an excess of boron.

The work of Schissel and Trulson<sup>54</sup> yields a value for the heat of formation also in general agreement with the above. The value



obtained is dependent on choice of heat of sublimation of boron. It appears that a choice of  $\Delta H_{f,298, \text{TiB}_2}^\circ = -65 \text{ kcal/mole}$  and  $\Delta H_{298, \text{B, sub}}^\circ = 132 \text{ kcal/mole}$  fits their data reasonably well. Thus from two independent determinations by vaporization studies, a heat of formation for  $\text{TiB}_2$  is obtained which is in fairly good agreement with the calorimetric data. Also the nitride equilibria of Williams<sup>38</sup> yield  $\Delta H_{f,298}^\circ = -70.26 \text{ kcal/mole}$ , in good agreement with the calorimetric value.

It is suggested that the probable accuracy of the heat of formation of  $\text{TiB}_2$  is  $\pm 3.0 \text{ kcal/mole}$  thus giving as the accepted value  $\Delta H_{f,298, \text{TiB}_2}^\circ = -66.85 \pm 3.0 \text{ kcal/mole}$ . The preferred value for the heat of sublimation of  $\text{TiB}_2$  is the experimental value of Schissel and Trulson<sup>54</sup> as recomputed here; namely,  $\Delta H_{298}^\circ = 441.5 \text{ kcal/mole}$ .

#### 4) Table preparation and normal boiling point

From the data already chosen, thermodynamic tables have been prepared. From these tables, it is found that the free energy of formation for  $\text{TiB}_2$  from its reference elements becomes zero at about  $4260^\circ\text{K}$ . At this temperature, both boron and titanium exist as gaseous elements, and hence the free energy of formation refers to formation of  $\text{TiB}_2$  from gaseous Ti and B. Thus, it is found that, assuming the vaporization to be congruent at the stoichiometric composition,  $P_{\text{B}} = 1.26 \text{ atm}$  and  $P_{\text{Ti}} = 0.63 \text{ atm}$  at  $4260^\circ\text{K}$ . The normal boiling point at 1 atm for  $\text{TiB}_2$  would be slightly lower than this temperature and is found to be approximately  $4100^\circ\text{K}$ . Hence, data tabulated above  $4100^\circ\text{K}$  in the table refer to a metastable state as far as  $\text{TiB}_2$  is concerned when the external pressure is less than 1 atm. The normal boiling point of  $4100^\circ\text{K}$  obtained herein must be considered to have a sizable uncertainty of, perhaps,  $\pm 200^\circ\text{K}$ .

#### Supplement

Kaufman and Clougherty<sup>58</sup> have published the experimental data for  $\text{TiB}_2$  found by Westrum.<sup>25</sup> The results give  $S_{298.15}^\circ = 6.808 \text{ e.u.}$  in good agreement with the estimates used in this work.

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## 30.2 Titanium Carbides

### Phase Diagrams and General Behavior

A phase diagram shown by Hansen and Anderko<sup>1</sup> is based on the work of Cadoff and Nielsen.<sup>2</sup> According to this work, a single compound, TiC, of variable composition is formed. Hansen and Anderko<sup>1</sup> also note that a compound Ti<sub>2</sub>C had been suspected but could not be found. More recently (1962), Raman and Ramachandran<sup>3</sup> have presented evidence for a new carbide, titanium bicarbide, TiC<sub>2</sub>. They found this compound to be simple cubic with a lattice parameter,  $a = 3.13\text{\AA}$ . As yet, there appears to have been no confirmation of this carbide.

Storms<sup>4</sup> has reviewed available phase-diagram data for the Ti-C system in 1962 and presented a diagram quite similar to that of Cadoff and Nielsen.<sup>2</sup> Storms prefers eutectic melting behavior at TiC<sub>0.046</sub>, based on the observations of Bickerdike and Hughes.<sup>5</sup> Storms<sup>4</sup> shows a melting maximum to occur at a composition of about TiC<sub>0.87</sub>, whereas the diagram published by Hansen and Anderko<sup>1</sup> shows the maximum at TiC<sub>1.0</sub>.

In the present work, effort will be restricted to obtaining data for the TiC compound. This is the most refractory, and the only compound well confirmed by many investigations.

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### 30.2.1 Titanium Carbide (TiC(s, l))

#### a. Crystal Structure and Melting Point

Hansen and Anderko<sup>1</sup> indicate that TiC has a face-centered cubic structure (NaCl type). There are 4 molecules per cell and the lattice parameter is  $a = 4.329 \pm 0.001 \text{ \AA}$ . McQuillan and McQuillan<sup>2</sup> cite the work of Ehrlich,<sup>3</sup> which indicates that the lattice parameter increases smoothly as the carbon content increases from 22 to 50 atom-percent carbon.

Storms<sup>4</sup> notes that TiC has a wide homogeneity range. Lower limits at TiC<sub>0.28</sub> have been reported by Ehrlich,<sup>3</sup> Rengstorff,<sup>5</sup> and Ragone,<sup>6</sup> but Storms believes oxygen impurities are responsible for such a low limit. He prefers the lower-limit value of TiC<sub>0.49</sub> found by Cadoff and Nielsen.<sup>7</sup> This lower limit applies at a temperature of 1645°C. The upper limit for the TiC phase is considered to be TiC<sub>1.0</sub>, but the exact value is not certain.

Melting points of 2940°C (3213°K) by Engelke et al,<sup>8</sup> 3160°C (3433°K) by Friederich and Sittig,<sup>9</sup> 3140°C (3413°K) by Agte and Moers,<sup>10</sup> 3030°C (3303°K) by Geach and Jones,<sup>11</sup> and 3250°C (3523°K) by Schwarzkopf and Kieffer<sup>12</sup> have been reported. It is difficult to determine a precise value. In the present work the more recent value of Engelke et al<sup>8</sup> has been accepted.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at 298.15°K

Low-temperature heat-capacity data for TiC have been compiled by Kelley and King,<sup>13</sup> based on the original work of Kelley<sup>14</sup> for the range 55.1° to 295°K. The data lead to

$$C_{p, 298.15}^{\circ} = 8.04 \text{ cal degK}^{-1} \text{ gfw}^{-1},$$

$$\text{and } S_{298.15}^{\circ} = 5.79 \pm 0.05 \text{ e. u.}$$

In the present work, the original Kelley<sup>14</sup> data have been integrated to give  $H_{298.15}^{\circ} - H_0^{\circ} = 1.101 \text{ kcal/mole}$ . This includes a contribution of  $H_{55.1}^{\circ} - H_0^{\circ} = 0.004 \text{ kcal/mole}$  estimated from the Debye equation proposed by Kelley.

## 2) High-temperature heat content

Kelley<sup>15</sup> tabulates a heat-capacity relation for TiC based on the work of Naylor.<sup>16</sup> The data have been obtained by drop calorimetry for the range 298° to 1735°K. The equation obtained is

$$C_p^\circ = 11.83 + 0.80 \times 10^{-3}T - 3.58 \times 10^5 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

More recent data for TiC have been obtained at Southern Research Institute (SRI) by Pears et al.<sup>17</sup> They have used drop calorimetry over the range 603° to 4750°F (590.3° to 2894°K). A summary of their data, converted to cgs units, is shown below.

### HEAT-CONTENT DATA OF PEARS et al CONVERTED\* TO cgs UNITS

T (°K)	$H_T^\circ - H_{298}^\circ$ (cal/mole)
590.3	2713
933	7326
995	8590
1024	7176
1363	12568
1385	13117
1644	16662
1938	20606
2216	25366
2449	29127
2477	28028
2477	30358
2649	33420
2769	34019
2841	36316
2894	35584

\*A value of  $H_{298.15} - H_{273.15} = 196$  cal/mole has been used in making the conversion. This value has been determined by integration of the Kelley<sup>14</sup> low-temperature data.



A treatment of the Pears et al<sup>17</sup> enthalpy data by the Shomate method using  $C_p^\circ, 298.15 = 8.04 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  leads to the equation

$$C_p^\circ = 10.173 + 0.268 \times 10^{-2}T - 0.2606 \times 10^6 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation when integrated can reproduce the experimental enthalpies to 11.6 percent or better.

Another method to derive a heat-capacity equation for TiC has involved a Shomate treatment of the enthalpy contents reported by Naylor<sup>16</sup> and by Pears et al.<sup>17</sup> The equation derived is

$$C_p^\circ = 11.114 + 0.1919 \times 10^{-2}T - 0.3241 \times 10^6 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

This equation leads to enthalpy contents larger than the experimental ones reported by Naylor in the range 790° to 1735°K. The maximum deviation in enthalpy values obtained by the above equation is 12.8 percent at 1024°K for the SRI data.

In view of the relatively wide spread of the SRI (Pears et al<sup>17</sup>) data, and because of the better internal agreement of the Naylor<sup>16</sup> data, the latter data have been accepted here. Thus the equation,

$$C_p^\circ = 11.83 + 0.80 \times 10^{-3}T - 3.58 \times 10^5 T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1},$$

is accepted and is extrapolated to the melting point.

It may be of interest to compare free-energy functions obtained by various methods as shown in table 64.

TABLE 64  
COMPARISON OF FREE-ENERGY FUNCTIONS FOR TiC  
(cal degK<sup>-1</sup>gfw<sup>-1</sup>)

T (°K)	Present Work (i. e. , Naylor Data)	SRI <sup>17</sup> Plus Naylor <sup>16</sup> Data	SRI <sup>17</sup> Data
298.15	5.79	5.79	5.79
1000	11.008	11.014	10.899
2000	17.361	17.556	17.375
3000	21.789	22.297	22.187

From the data in table 64 it is seen even different choices of data lead to relatively small changes in free-energy functions.

At the melting point of TiC, it has been assumed that the heat of fusion is 20 kcal/mole. The heat capacity of liquid TiC has been estimated to be  $16.0 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ .

### 3) Heat of formation

Humphrey<sup>18</sup> has measured the heat of combustion of a sample of TiC and has reported a heat of formation,

$$\Delta H_{f298.15}^{\circ} = -43.85 \pm 0.39 \text{ kcal/mole.}$$

The sample of TiC used had contained 99 percent TiC, 0.40 percent Ti, 0.26 percent Si, and 0.34 percent other impurities. Humphrey has used a heat-of-formation value for TiO<sub>2</sub> of -225.52 kcal/mole in reducing his data. Using the value -225.8 kcal/mole for TiO<sub>2</sub> accepted in the present work, a corrected heat of formation for TiC is obtained as -44.13 kcal/mole.

Another calorimetric determination has been reported by Morozova, Khripun, and Ariya.<sup>19</sup> For a sample of TiC which had been prepared at 1900°C, they obtained a heat of formation of -46 kcal/mole in good agreement with Humphrey. However for a sample prepared at a higher temperature, they obtained a much more negative enthalpy of formation; i. e., -55 kcal/mole. Morozova et al<sup>19</sup> preferred the latter value as the heat of formation for TiC at 298.15°K.

Electrochemical experiments have been reported by Smirnov and Krasnov,<sup>20</sup> which give  $\Delta H_{f298.15}^{\circ} = -54.0 \text{ kcal/mole}$  for the TiC heat-of-formation value.

Vaporization studies of TiC at high temperatures have been reported by Chupka et al,<sup>21</sup> Fujishiro and Gokcen,<sup>22</sup> Coffman et al,<sup>23</sup> and Bolgar, Verkhoglyadova, and Samsonov.<sup>24</sup>

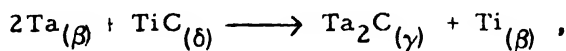
The studies by Chupka et al<sup>21</sup> utilized a mass spectrometer to show that the important gaseous species are atomic ones; i. e., molecular species are unimportant. Their data yielded an approximate heat-of-formation value for TiC of -45.5 kcal/mole in general agreement with the Humphrey<sup>18</sup> value. Knudsen effusion was used by Fujishiro and Gokcen to obtain  $\Delta H_{f298.15}^{\circ} = -31.333 \text{ kcal/mole}$ . This value appears to be too positive in view of the other work.

Coffman et al<sup>23</sup> have reported vaporization studies which utilized both Langmuir weight losses and atomic absorption spectroscopy. From the Langmuir evaporation studies, a heat of formation,  $\Delta H_{f298.15}^{\circ} = -42.8 \pm 1.2$  kcal/mole, was calculated. In good agreement with this, the resonance-line absorption studies yielded  $-42.73 \pm 0.5$  kcal/mole. The work by Bolgar et al<sup>24</sup> appears subject to serious error since the authors indicated that molecular species were produced by the vaporization.

Equilibrium studies of the Ti-C-O system have been made by Brantley and Beckman,<sup>25</sup> Nishimura and Kimura,<sup>26, 27</sup> Meerson and Krein,<sup>28</sup> Meerson and Lipkes,<sup>29</sup> and Kutsev and Ormont.<sup>30</sup> Because of the formation of  $TiC_xO_y$  solid solutions, evaluation of the heat of formation of TiC is not as simple as has been proposed by Brantley and Beckman.<sup>25</sup> These authors have claimed to have found  $TiO_2$  existing in equilibria with TiC, carbon, and CO(gas). However, Meerson and Krein<sup>28</sup> have noted that it is not possible for this to occur by phase-rule considerations.

A high-temperature calorimetric reaction of titanium with carbon was studied by Lowell and Williams.<sup>31</sup> They found  $\Delta H_{f298.15}^{\circ} = -45.5 \pm 4.6$  kcal/mole in agreement with the Humphrey data.<sup>18</sup>

Equilibria in the Ti-Ta-C system have been reported by McMullin and Norton.<sup>32</sup> As reported earlier by Barriault et al<sup>33</sup> at 1820°C, the free energy for the reaction,



has been calculated assuming Raoult's law to apply. This has yielded

$$\Delta F_{20930K}^{\circ} = -4232 \text{ cal/mole.}$$

From the given reaction, then,

$$\begin{aligned}\Delta F_{TiC, 20930K}^{\circ} &= \Delta F_{Ta_2C}^{\circ} - (-4232), \\ &= -44,859 + 4232, \\ &= -40,627 \text{ cal/mole or } -40.627 \text{ kcal/mole.}\end{aligned}$$

In the above calculation, data for  $Ta_2C$  have been taken from the present compilation. Using free-energy functions from this work, it is then found that

$$\Delta H_{f298.15, \text{TiC}}^{\circ} = -40,627 + 2093 (-3.212),$$

$$= -47,349 \text{ cal/mole or } -47.349 \text{ kcal/mole.}$$

Thus, the value calculated from the McMullin and Norton equilibria<sup>32</sup> is seen to yield a result in good agreement with the Humphrey value.<sup>18</sup>

In reviewing the available heat-of-formation data, it is seen that a considerable range of values has been reported. However, it is believed that the most likely value is in the range -43 to -48 kcal/mole. In view of the generally good accuracy of calorimetric data, the Humphrey corrected value of -44.13 kcal/mole is accepted.

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### 30.3 Titanium Nitrides

#### Phase Diagram and General Information

In the Ti-N phase diagram by Hansen and Anderko,<sup>1</sup> the "TiN" phase with a very wide homogeneity range is the most important. The  $\epsilon$ -phase with a nominal composition of  $Ti_3N$  is shown to be stable below  $1050^\circ C$ , but it has not been definitely confirmed. Storms<sup>2</sup> shows a phase diagram similar to that of Hansen and Anderko, and also based on the original work of Palty et al.<sup>3</sup>

More recently, Nowotny et al.<sup>4</sup> have suggested that the  $\epsilon$ -phase has the nominal composition  $Ti_2N$ . Holmberg<sup>5</sup> has confirmed this and found the phase to be tetragonal with a structure of the antirutile type. The  $Ti_2N$  phase has a narrow region of homogeneity at  $TiN_{0.5}$ . Holmberg also finds that the lower limit of the homogeneity range for the TiN phase is at  $TiN_{0.6}$ , which is considerably higher than indicated by earlier works.

Thus, aside from the terminal-metal solid solutions, the only compound phases in the Ti-N system are TiN and possibly  $Ti_2N$ . Only the first; i. e., TiN, is sufficiently well characterized to permit preparation of a thermodynamic table.

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#### 30.3.1 Titanium Nitride ( $TiN_{(s, \ell)}$ )

##### a. Crystal Structure and Melting Point

From the works of Hansen and Anderko,<sup>1</sup> Storms,<sup>2</sup> and Palty et al.,<sup>3</sup> it is found that the TiN phase has a cubic structure (NaCl type). The

lattice parameter has been observed to vary from 4.22 Å at the lower limit of the homogeneity range to a maximum of 4.243 Å at the stoichiometric composition. Further addition of nitrogen causes the parameter to decrease to 4.221 Å at 53.7 atom-percent N. This leads to the conclusion made by Brager<sup>4</sup> that the solid solution on both sides of the stoichiometric composition is of the subtraction type. Thus, the upper limit is caused by vacancies in both the Ti and N lattices.

Storms<sup>2</sup> notes that, for the series of nitrides TiN, ZrN, and HfN, the behavior of lattice parameter for TiN as nitrogen is added is normal, whereas ZrN and HfN exhibit anomalous behavior. For the latter compounds, the lattice parameter decreases as nitrogen is added.

The limits of the homogeneity range for the TiN phase are not well known. Palty *et al*<sup>3</sup> found the lower limit to be TiN<sub>0.38</sub>, and Brager<sup>4</sup> found the upper limit near TiN<sub>1.16</sub>. Such a homogeneity range is indeed a wide one. More recently, Holmberg<sup>5</sup> has placed the lower phase limit at TiN<sub>0.6</sub>, Vainshtein *et al*<sup>6</sup> considered the range to be TiN<sub>0.45</sub> to TiN<sub>0.99</sub>. Gorbunov *et al*<sup>7</sup> have reported neutron-diffraction studies for the Ti<sub>0.85</sub>N (TiN<sub>1.18</sub>) composition. Miscellaneous properties for titanium nitride have been reported by Samsonov.<sup>8,9</sup>

Phillipp<sup>10</sup> performed electrochemical studies on TiN to show that it has metallic bonding. Pearson<sup>11</sup> concurs with this conclusion, using considerations of structural chemistry. Pearson also notes that covalent-metallic sizes apply to TiN which is considered to be an interstitial metallic phase of the Hägg type. On the other hand, TiO is much more ionic, and hence ionic radii describe its properties.

Melting points of 2950° ± 50°C (3223°K) by Agte and Moers,<sup>12</sup> and 2930°C (3203°K) by Friederich and Sittig,<sup>13</sup> have been reported. In the present work, the Agte and Moers value is accepted.

## b. Thermodynamic Properties

### 1) Entropy and heat content at 298.15°K

Kelley and King<sup>14</sup> indicate that the only experimental low-temperature heat-capacity data are those by Shomate<sup>15</sup> for the range 52° to 297°K. These data lead to  $S_{298.15}^{\circ} = 7.24 \pm 0.04$  e. u. A recomputation of the Shomate data in the present work leads to  $H_{298.15}^{\circ} - H_0^{\circ} = 1.310$  kcal g<sup>-1</sup>.



## 2) High-temperature heat capacity

Kelley<sup>16</sup> tabulates a high-temperature heat-capacity equation and cites the work of Naylor<sup>17</sup> for the range 298° to 1738°K and the work of Sato<sup>18</sup> for the range 273° to 773°K. The equation obtained by Kelley<sup>16</sup> is

$$C_p^\circ = 11.91 + 0.94 \times 10^{-3}T - 2.96 \times 10^5 T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1},$$

for the range  $298.15^\circ\text{K} \leq T \leq 2000^\circ\text{K}$ .

Neel et al<sup>19</sup> made enthalpy measurements in the range 499° to 4650°F (532° to 2838°K). They had derived a heat-capacity equation by least-squares fit but revised their calculations in a later work by Pears et al.<sup>20</sup> In the present work, the original enthalpy data of Neel et al<sup>19</sup> have been converted to cgs units and are shown below. A small correction of  $H_{298.15}^\circ - H_{273.15}^\circ = 216 \text{ cal gfw}^{-1}$  was used to correct the data to a 298.15°K reference temperature. The correction was obtained by integration of the Shomate<sup>15</sup> low-temperature data.

### ENTHALPY DATA FOR TiN CONVERTED TO cgs UNITS FROM NEEL et al<sup>19</sup>

T	$H_T^\circ - H_{298.15}^\circ$
°K	cal gfw <sup>-1</sup>
532.5	2291.3
830.9	5458.8
1093.1	8795.0
1373.7	12234.3
1649.8	17496.5
1877.5	22242.8
2144.2	25888.5
2422.0	30669.1
2838.7	35896.9

Using  $C_p^\circ = 8.86 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  from the low-temperature data and using the Shomate method, a heat-capacity equation was derived:

$$C_p^\circ = 8.4453 + 0.43385 \times 10^{-2}T - 0.78126 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1},$$

This equation (when integrated) fits the experimental enthalpy to within 8.1 percent.

Since the Kelley equation gives a better fit to the enthalpy data used in its derivation (i. e., Naylor data), it is believed that it should be given greater weight. Therefore, the Kelley equation is used in the present work and is extrapolated to the melting point.

At the melting point, the heat of fusion is estimated to be 15.0 kcal gfw<sup>-1</sup>. For liquid TiN, the heat capacity is estimated to be 16.0 cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

### 3) Heat of formation

Humphrey<sup>21</sup> used oxygen-bomb calorimetry to find a heat of formation of  $-80.47 \pm 0.3 \text{ kcal gfw}^{-1}$ . The original work used a heat of formation of  $-225.52 \text{ kcal gfw}^{-1}$  for TiO<sub>2</sub>. When it is corrected, using this tabulation<sup>1</sup> value of  $-225.8 \text{ kcal gfw}^{-1}$ , the heat of formation for TiN becomes  $-80.75 \text{ kcal gfw}^{-1}$ . Neumann et al<sup>22</sup> had found  $\Delta H_{f298.15}^\circ = -80.3 \text{ kcal gfw}^{-1}$ . Hoch et al<sup>23</sup> obtained  $\Delta H_{f298.15}^\circ = -79.4 \text{ kcal gfw}^{-1}$  via vaporization studies. In the present work, the corrected Humphrey value of  $-80.75 \text{ kcal gfw}^{-1}$  is used.

### 4) Vaporization studies

Vaporization studies for TiN have been performed by Hoch et al,<sup>23</sup> Dreger and Margrave,<sup>24</sup> Akishin and Khodiev,<sup>25</sup> and Fesenko and Bolgar.<sup>26</sup> The vaporization proceeds to form the gaseous elements. There does not appear to be a congruently vaporizing composition. Spectroscopic studies have been reported by Parkinson and Reeves.<sup>27</sup>

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### 30.4 Titanium Oxides

#### Phase Diagram and General Behavior

A phase diagram for the Ti-O system from 0 to 60 atom-percent oxygen is given by Hansen and Anderko.<sup>1</sup> An even more extended diagram to 66.7 atom-percent oxygen ( $\text{TiO}_2$ ) is given by DeVries and Roy,<sup>2</sup> and compiled by Levin et al.<sup>3</sup> These works show the lowest oxide as either a  $\text{Ti}_4\text{O}_3$  or  $\text{Ti}_3\text{O}_2$  phase, but the data are considered somewhat tentative. The TiO phase is well established. Higher oxides shown by these works include  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ , and  $\text{TiO}_2$ .

Subsequent to the above work, Andersson et al.<sup>4</sup> have identified the following phases:  $\text{Ti}_2\text{O}$ , TiO (low-temperature form),  $\text{Ti}_4\text{O}_7$ ,  $\text{Ti}_5\text{O}_9$ ,  $\text{Ti}_6\text{O}_{11}$ ,  $\text{Ti}_7\text{O}_{13}$ ,  $\text{Ti}_8\text{O}_{15}$ ,  $\text{Ti}_9\text{O}_{17}$ , and  $\text{Ti}_{10}\text{O}_{19}$ . Andersson et al.<sup>4</sup> note that the latter group of compounds (i. e.,  $\text{Ti}_4\text{O}_7$  and later ones) have the general formula  $\text{Ti}_n\text{O}_{2n-1}$  and form a homologous series of structurally interrelated compounds based on the rutile-type structure. Further data on the titanium oxides have been obtained by Magneli et al.<sup>5</sup>

In their studies, Andersson et al.<sup>4</sup> have annealed high-oxygen samples (i. e.,  $\text{TiO}_{1.5}$  to  $\text{TiO}_2$ ) at  $1150^\circ\text{C}$  and then quenched them. Their studies show the following homogeneity ranges:

Phase	Composition Range
TiO	$\text{TiO}_{0.64}$ to $\text{TiO}_{1.25}$
$\text{Ti}_2\text{O}_3$	$\text{Ti}_{0.49}$ to $\text{Ti}_{1.51}$
$\text{Ti}_3\text{O}_5$	$\text{Ti}_{1.67}$ (no appreciable range)
$\text{TiO}_2$	$\text{Ti}_{1.95}$ to $\text{TiO}_2$

Hoch et al.<sup>6</sup> note that Hurlen<sup>7</sup> has stated that the compounds  $\text{Ti}_n\text{O}_{2n-1}$  are ordered structures. These ordered structures will become disordered at higher temperatures of about  $1500^\circ\text{C}$  and decompose into a 2-phase  $\text{Ti}_3\text{O}_5$  -  $\text{TiO}_2$  region.

Additional data regarding possible  $\text{Ti}_6\text{O}$  and  $\text{Ti}_3\text{O}$  compounds have been given by Kornilov and Glazova.<sup>8</sup>

From this brief resume, it is clear that there are still many unresolved questions in this Ti-O system. In this present compilation, data are compiled for the more adequately confirmed compounds; i. e., TiO,  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ , and  $\text{TiO}_2$ . Further work will be required to define the ranges of stability for the other compounds discussed.

It may also be noted that Bogdanova et al.<sup>9</sup> by a study of  $H_2/H_2O$  pressure ratios at 1030°C found 6 adjoining phases (no intervening 2-phase regions). They also have found from electric-conductivity studies evidence in support of the  $Ti_3O_5$ ,  $Ti_4O_7$ ,  $Ti_6O_{11}$ ,  $Ti_8O_{15}$ , and  $Ti_{10}O_{19}$  phases found by Andersson et al.<sup>4</sup> Yakovleva and Ariya<sup>10</sup> have considered the possibility of studying emf relationships. Lecerf<sup>11</sup> has studied properties of  $TiO$  and  $Ti_2O_3$ . Makarov and Kuznetsov<sup>12</sup> have studied the crystal structure and nature of the lower oxides from  $Ti$  to  $TiO_{0.48}$ .

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### 30.4.1 Titanium Monoxide ( $\text{TiO}_{(s, l)}$ )

#### a. Crystal Structure, Transition Point, and Melting Point

According to Ehrlich,<sup>1</sup> titanium monoxide has the f. c. c. NaCl (B1) type of structure. Random vacancies in both the titanium and oxygen lattices occur. At the  $\text{TiO}_{1.00}$  composition, 15 percent of both Ti and O positions are vacant.

Andersson et al<sup>2</sup> have found the TiO phase to have a wide homogeneity range  $\text{TiO}_{0.64}$  to  $\text{TiO}_{1.25}$ .

Evidence for a phase transition at  $991^{\circ}\text{C}$  ( $1264^{\circ}\text{K}$ ) has been obtained from the heat-capacity measurements of Naylor.<sup>3</sup> Wang and Grant,<sup>4</sup> and Kuylensstierna and Magneli,<sup>5</sup> have noted that annealing the high-temperature form of TiO (NaCl type) at a low temperature ( $925^{\circ}$  and  $1800^{\circ}\text{C}$ ) causes transitions to a TiO phase and a complicated pattern. Andersson et al<sup>2</sup> suggest that the low-temperature modification of TiO may have an ordered arrangement of the random atomic vacancies present in TiO (NaCl type). Smagina and Kutsev<sup>6</sup> have calculated the degree of disorder in the TiO phase. Hoch<sup>7</sup> has related the appearance of a superstructure in TiO at low temperatures to the presence of the vacancies. Hoch proceeds to calculate the critical temperature of ordering as  $923^{\circ} \pm 75^{\circ}\text{K}$  which is lower than the experimental value of  $800^{\circ}\text{C}$  ( $1073^{\circ}\text{K}$ ) by Magneli et al.<sup>8</sup> It may be noted that Hoch used a zero-order approximation, and hence the calculation is not a precise one.

Hoch, Iyer, and Nelken<sup>9</sup> have made emf measurements in a solid electrolyte cell and have deduced phase limits for the TiO phase in good agreement with Bumps, Kessler, and Hansen,<sup>10</sup> and Schofield and Bacon.<sup>11</sup> At  $1275^{\circ}\text{K}$ , the oxygen mole-fraction limits are 0.4721 and 0.5567; i. e.,  $\text{TiO}_{0.894}$  to  $\text{TiO}_{1.255}$ . It may be noted that the lower limit is in disagreement with that found by Andersson et al.<sup>2</sup>

Additional comments on the structure of titanium monoxide have been made by Ariya and Popov,<sup>12</sup> Kaufman,<sup>13</sup> and Andersson.<sup>14</sup> A transition in the TiO phase has been found by Schofield and Bacon<sup>11</sup> in the range  $950^{\circ}$  to  $1000^{\circ}\text{C}$  in agreement with Naylor's<sup>3</sup> value of  $990^{\circ}\text{C}$ .

In the present work, it has been considered that TiO undergoes a phase change at  $1264^{\circ}\text{K}$  as found by Naylor.<sup>3</sup>

According to Schofield and Bacon,<sup>11</sup> the solidus for the  $\text{TiO}_{1.0}$  composition is at  $1720^{\circ}\text{C}$  ( $1993^{\circ}\text{K}$ ), and the liquidus is at  $1770^{\circ}\text{C}$  ( $2043^{\circ}\text{K}$ ). Brewer<sup>15</sup> lists a decomposition point of  $2010^{\circ}\text{K}$  for  $\text{TiO}$ . Melting points of  $2023^{\circ}\text{K}$  by Dawihl et al.,<sup>16</sup>  $2023^{\circ}\text{K}$  by Nishimura et al.,<sup>17</sup> and  $2103^{\circ}\text{K}$  by DeVries et al.<sup>18</sup> have also been given. In the present work, the Brewer value at  $2010^{\circ}\text{K}$  has been accepted as a melting point. The incongruent melting behavior actually observed has been ignored in the present tabulations, and thermodynamic functions have been extrapolated to higher temperatures for the  $\text{TiO}_{1.0}$  composition.

## b. Thermodynamic Properties

### 1) Entropy and heat content at $298.15^{\circ}\text{K}$

Shomate<sup>19</sup> has obtained low-temperature heat-capacity data for the range  $52^{\circ}$  to  $297^{\circ}\text{K}$ . His data lead to  $S_{298.15}^{\circ} = 8.31 \pm 0.04$  e. u. An integration of this low-temperature data by JANAF<sup>20</sup> has yielded  $H_{298.15}^{\circ} - H_0^{\circ} = 1.473$  kcal/mole. Hoch et al.<sup>9</sup> show that the entropy of  $\text{TiO}$  should be increased by 1.68 e. u. to account for the randomness of vacant titanium and oxygen sites. Thus, the experimental low-temperature value of Shomate must be increased from 8.31 to 9.99 e. u. In the present work, the values  $S_{298.15}^{\circ} = 9.99$  e. u. and  $H_{298.15}^{\circ} - H_0^{\circ} = 1.473$  kcal/mole have been accepted.

### 2) High-temperature heat content

Naylor<sup>3</sup> has made heat-capacity measurements for the range  $298^{\circ}$  to  $1800^{\circ}\text{K}$ . For the range to the transition point; i. e.,  $298^{\circ}$  to  $1264^{\circ}\text{K}$ , he has obtained

$$C_p^{\circ} = 10.57 + 3.6 \times 10^{-3} T - 1.86 \times 10^{-5} T^2 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

Above  $1264^{\circ}\text{K}$ , he has found

$$C_p^{\circ} = 11.85 + 3.0 \times 10^{-3} T \text{ cal degK}^{-1} \text{ gfw}^{-1}$$

for the range  $1264^{\circ}$  to  $1800^{\circ}\text{K}$ .

General agreement with the above data has been obtained by Erofeeva et al.<sup>21</sup>

In the present work, the data of Naylor<sup>3</sup> have been utilized. A heat of transition of  $\Delta H_{1264}^{\circ} = 820$  cal/mole has also been accepted.



The heat of fusion has been estimated to be  $14.0 \pm 2.0$  kcal/mole from Kubaschewski and Evans.<sup>22</sup>

Above the melting point of TiO, it has been assumed that the heat capacity is constant and equal to  $14.5 \text{ cal degK}^{-1} \text{ gfw}^{-1}$ .

### 3) Heat of formation

Combustion calorimetry has been used by Humphrey<sup>23</sup> to obtain a standard heat of formation of  $\Delta H_{f298.15}^\circ = -123.91 \pm 0.28$  kcal/mole. Mah et al<sup>24</sup> have obtained  $\Delta H_{f298.15}^\circ = -124.2$  kcal/mole. A later publication by Kelley and Mah<sup>25</sup> tabulates the value  $\Delta H_{f298.15}^\circ = -124.15$  kcal/mole based on Mah et al.<sup>24</sup> Ariya et al<sup>26</sup> have obtained a heat of formation of  $-125.4$  kcal/mole in good agreement with these other results. They have studied several compositions and have noted that a structural change may be evident near the stoichiometric  $\text{TiO}_{1.0}$  composition.

In the present work, the Mah et al,<sup>24</sup> and Kelley and Mah,<sup>25</sup> value of  $\Delta H_{f298.15}^\circ = -124.15$  kcal/mole, which is consistent with the heat-of-formation value for  $\text{TiO}_2$  used in the present tabulation, has been adopted.

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### 30.4.2 Titanium Monoxide ( $\text{TiO}_{(g)}$ )

#### a. Thermodynamic Functions

At the present time, several difficulties exist in obtaining a complete representation of the electronic energy levels for  $\text{TiO}_{(g)}$ . Herzberg<sup>1</sup> and Rosen<sup>2</sup> list  $X^3\pi$  state as the ground state. The  $a^1\Delta$  state is shown by Phillips<sup>3</sup> to be the next higher electronic state at  $581\text{ cm}^{-1}$  above the ground state. However, he could only determine its position to a low degree of accuracy. Thus, the possible values of this term could range from  $274$  to  $804\text{ cm}^{-1}$ . Phillips made his studies by observing the emission spectrum of  $\text{TiO}$  from  $4500$  to  $8000\text{ \AA}$  using a King furnace. Intensity measurements at different temperatures have made it possible to relate the relative positions of the two states. Additional higher states have been reported by Pettersson and Lindgren,<sup>4</sup> who have studied the  $b^1\pi$ - $d^1\Sigma$  transition. They have reported the  $d^1\Sigma$  state to be low lying with a term value of  $1708\text{ cm}^{-1}$ , while the  $b^1\pi$  state has a term value of  $10814.4\text{ cm}^{-1}$ . They have also indicated that an  $a^1\Sigma$  state is located between the  $d^1\Sigma$  and  $b^1\pi$  states. Additional higher states are known but are not considered here since their contributions would be small compared to the uncertainties, of the low-lying states. An example of this uncertainty is the fact that Berg and Sinanoglu<sup>5</sup> have shown by a theoretical analysis that the expected ground state is the  $^3\Sigma$  state rather than the  $^3\pi$  accepted by Herzberg<sup>1</sup> and Rosen<sup>2</sup>. Berg and Sinanoglu<sup>5</sup> state that the  $^1\Sigma$  is expected to be  $\sim 8300\text{ cm}^{-1}$  above the ground state  $^3\Sigma$ , and the  $^3\pi$  state would be  $16000\text{ cm}^{-1}$  above the ground state.

For the purpose of preparing thermodynamic tables, it is preferred here to use the experimental determinations already cited. That is, the ground state is considered to be  $X^3\pi$ , and the other higher states  $a^1\Delta$ ,  $d^1\Sigma$ , and  $b^1\pi$  are included. The choice of data corresponds to case HS-67 in section IIIA, and is shown on the following page in table 65 for convenience.

TABLE 65  
SPECTROSCOPIC DATA USED FOR  
TITANIUM MONOXIDE CALCULATIONS

Electronic state	$X^3\Pi$			$a^1\Delta$	$d^1\Sigma$	$b^1\Pi$
$E$ (cm <sup>-1</sup> )	0.0	66.7	141.3	581.0	1708.0	10814.0
$g$	2.0	2.0	2.0	2.0	1.0	2.0
$\omega_e$ (cm <sup>-1</sup> )	1008.6	1008.6	1008.6	1009.6	1023.8	918.7
$\omega_e x_e$ (cm <sup>-1</sup> )	4.61	4.61	4.61	0.0	4.64	3.75
$\omega_e y_e$ (cm <sup>-1</sup> )	0.0	0.0	0.0	0.0	0.0	0.0
$B_e$ (cm <sup>-1</sup> )	0.5355	0.5355	0.5355	0.5362	0.5490	0.513
$\alpha_e$ (cm <sup>-1</sup> )	0.0031	0.0031	0.0031	0.0	0.00337	0.0029
$\gamma_e$ (cm <sup>-1</sup> )	0.0	0.0	0.0	0.0	0.0	0.0
$D_e$ (cm <sup>-1</sup> )	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.03 \times 10^{-7}$	$6.04 \times 10^{-7}$	0.0	0.0

For the ground state  $X^3\Pi$ , the spectroscopic constants  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ , and  $\alpha_e$  are from Herzberg.<sup>1</sup> However,  $\omega_e$  has been corrected from 1008.4 to 1008.6 cm<sup>-1</sup> to compensate for the natural isotopic mixture.

$D_e$  is estimated from the relation  $D_e = \frac{4 B_e^3}{\omega_e^2}$ .

For the  $a^1\Delta$  state, the values of  $\omega_e$ ,  $B_e$ , and  $D_e$  are estimated. The value of  $r_e = 1.619\text{\AA}$  is taken from Herzberg<sup>1</sup> and used to calculate  $B_e$ . Also by using the relation  $r_e^2 \omega_e = \text{constant}$  for all electronic states of a given molecule, it has been possible to calculate  $\omega_e$ . Finally,  $D_e$

is estimated from the relation  $D_e = \frac{4 B_e^3}{\omega_e^2}$ . In the case of the

$d^1\Sigma$  and  $b^1\Pi$  states, the values of  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ , and  $\alpha_e$  have been taken from Pettersson and Lindgren.

It is of interest to compare the present calculations with those of other workers. Papousek<sup>6</sup> calculated data for the range of 50° to 2500°K considering only the  $X^3\Pi$  ground state. JANAF<sup>7</sup> has tabulated data again by considering only the  $X^3\Pi$  state. In the comparison, it is noted in table 66 that the present calculations give somewhat larger values for the entropy reflecting primarily the effect of additional electronic states.

TABLE 66  
COMPARISON OF VARIOUS SOURCES OF DATA FOR  
TITANIUM MONOXIDE (gas)  
(All Quantities in cal deg K<sup>-1</sup> gfw<sup>-1</sup>)

Temperature °K	Present Calculations		Papousek <sup>6</sup>		JANAF <sup>7</sup>	
	C <sub>p</sub> <sup>°</sup>	S <sup>°</sup>	C <sub>p</sub> <sup>°</sup>	S <sup>°</sup>	C <sub>p</sub> <sup>°</sup>	S <sup>°</sup>
1000	8.941	66.221	8.714	65.640	8.695	65.649
2000	9.097	72.482	8.975	71.781	8.967	71.783
2500	9.146	74.517	9.051	73.801	9.023	73.790
3000	9.205	76.190			9.065	75.439
4000	9.330	78.857			9.134	78.057
5000	9.439	80.953			9.195	80.102
6000	9.526	82.686			9.252	81.783

#### b. Heat of Formation

A complete self-consistent analysis of the heat-of-formation data for TiO(g) had not been completed at report time. JANAF<sup>7</sup> had listed a heat-of-formation value  $\Delta H_{f298.15}^\circ = 15.1 \pm 5$  kcal gfw<sup>-1</sup>. A preliminary value of the heat of sublimation for TiO(g),  $\Delta H_{298.15}^\circ$ , sublimation<sup>=</sup> 136.344 kcal gfw<sup>-1</sup> was derived from the vapor-pressure data of Groves, Hoch, and Johnston.<sup>8</sup> This gave a heat of formation of  $\Delta H_{f298.15}^\circ = 12.144$  kcal gfw<sup>-1</sup>. For this analysis, some preliminary, unpublished, free-energy functions available at Avco RAD were used for TiO(solid). The vapor-pressure results of Berkowitz et al<sup>9</sup> yielded a heat of sublimation of TiO(g) from TiO(solid) of  $\Delta H_{298.15}^\circ = 137.281$  kcal gfw<sup>-1</sup>, and  $\Delta H_{298.15}^\circ$ , TiO(g), formation = +13.081 kcal gfw<sup>-1</sup>.

Brewer<sup>10</sup> quoted a heat of sublimation for  $\text{TiO(g)}$  of  $\Delta H_{298.15}^\circ = 135 \pm 1 \text{ kcal gfw}^{-1}$ , and a heat of dissociation  $D_0^\circ = 160 \pm 2 \text{ kcal gfw}^{-1}$  (6.937 e. u.) The results quoted by Brewer are based on an unpublished work by Gilles and Wheatley.<sup>11</sup>

To make possible a complete thermodynamic table, a provisional value of  $\Delta H_{298.15}^\circ = 13.0 \text{ kcal gfw}^{-1}$  has been accepted. It is probable that this value is subject to an uncertainty of about  $\pm 5 \text{ kcal gfw}^{-1}$ .

### c. Uncertainties

Uncertainties for  $\text{TiO(g)}$  have been estimated by running several trial calculations for  $C_p^\circ$ ,  $S^\circ - \left( \frac{F_T^\circ - H_{298}^\circ}{T} \right)$ , and  $H_T^\circ - H_{298.15}^\circ$  using different types of input data. The range in values obtained, after being rounded off, is taken as an indication of the uncertainty. Further details on these calculations can be found in section IIC3 of the present report.

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### 30.4.3 Titanium Dioxide ( $\text{TiO}_{2(s,l)}$ )

#### a. Phase Data and Melting Point

$\text{TiO}_2$  exists in several crystalline modifications including rutile, anatase, and brookite. Brewer<sup>1</sup> notes that both anatase and brookite are thermodynamically unstable. Hence, the following work is restricted to discussing the stable rutile modification, which has a tetragonal structure. Brewer further notes that  $\text{TiO}_2$  has a homogeneity range of  $\text{TiO}_{1.9}$  to  $\text{TiO}_{2.0}$  which is compatible with its behavior as an n-type semiconductor.

Dorin and Tartakovskaya<sup>2</sup> have reduced  $\text{TiO}_2$  with titanium to produce specimens in the range of  $\text{TiO}_{1.99}$  to  $\text{TiO}_{1.93}$ .

There do not appear to be any known transitions for rutile into more stable structures.<sup>1,3</sup> Lashchenko and Kompanski<sup>4</sup> indicate a transition at 915 °K. Naylor<sup>5</sup> did not report a transition in his heat content measurements. We consider transitions to be nonexistent in this work.

Melting point data have been obtained by Brauer and Littke,<sup>6</sup> who noted that  $\text{TiO}_2$  loses  $\text{O}_2$  on heating to form  $\text{TiO}_{2-x}$ . As the oxygen pressure was increased, they noted that higher melting points were reached. A leveling off of melting points occurred when the  $\text{TiO}_{2.00}$  composition was maintained. Thus 1-atm  $\text{O}_2$  and higher  $\text{O}_2$  pressures held the composition at  $\text{TiO}_{2.00}$  for which a melting point of  $1870 \pm 15$  °C (2143 °K) was obtained. Diamond and Schneider<sup>7</sup> found a melting point of 1840 °C (2113 °K). Brewer<sup>1</sup> tabulates a melting point of  $2128 \pm 20$  °K.

St. Pierre<sup>8</sup> found a melting point of  $2113 \pm 10$  °K, and Bunting<sup>9</sup> found 2108 °K. In the present work, we accept the higher figures of Brauer and Littke.<sup>6</sup> Brewer<sup>1</sup> has noted that  $\text{TiO}_2$  decomposes at 3200°K.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at 298.15°K

Low-temperature heat capacity measurements have been made by Dugdale, Morrison, and Patterson<sup>10</sup> for the range (20° to 50 °K), McDonald and Seltz<sup>11</sup> (85 to 291 °K), and Shomate<sup>12</sup> (52.5 to 298.15°K). These works have been analyzed by Kelley and King<sup>13</sup> who found that  $S_{298.15}^\circ = 12.04 \pm 0.04$  eu., in good agreement with the value of  $12.01 \pm 0.05$  eu. reported by Shomate.<sup>12</sup> Since no value of  $H_{298.15}^\circ - H_0^\circ$  was reported by earlier workers, the original data of Shomate were integrated. Using his functions

$$C_p^\circ = D \left( \frac{318}{T} \right) + 2E \left( \frac{685}{T} \right)$$

to integrate the region 0 to 52.5 °K, it is found that  $S_{52.5}^\circ = 0.615$  eu and  $H_{52.5}^\circ - H_0^\circ = 24$  cal gfw<sup>-1</sup>. Finally,  $H_{298.15}^\circ - H_0^\circ = 2.064$  kcal gfw<sup>-1</sup> for TiO<sub>2</sub> is obtained. This value and  $S_{298.15}^\circ = 12.04 \pm 0.04$  eu from Kelley and King<sup>13</sup> are adopted in this work.

## 2) High-temperature heat content

Naylor<sup>5</sup> reported heat-content measurements from drop temperatures of 393.5 to 1746 °K. The Shomate method was used to derive an equation for heat capacity which could reproduce the experimental enthalpies within the mean percentage deviation of 0.2 percent. His equation is

$$C_p^\circ = 17.14 + 0.00098T - 3.50 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

Additional work by Arthur<sup>14</sup> for the range 295 to 1072 °K, and by Lietz<sup>15</sup> for the range 290 to 1283 °K, has been reviewed by Kelley<sup>16</sup> who obtained the equation

$$C_p^\circ = 17.97 + 0.28 \times 10^{-3}T - 4.35 \times 10^{-5}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}.$$

In the present work this equation has been accepted and extrapolated to the melting point.

At the melting point, the heat of fusion was estimated to be 15.0 kcal gfw<sup>-1</sup>. The uncertainty in this value is considered to be  $\pm 5$  kcal gfw<sup>-1</sup>.

Above the melting point, data have been extrapolated to 6000 °K, assuming that  $C_p^\circ = 18.475$  cal deg K<sup>-1</sup> gfw<sup>-1</sup>. Thus, it was assumed that liquid and solid heat capacities are equal at the melting point. As in many of the extrapolations on this project, the liquid phase may be metastable under atmospheric pressure conditions, since Brewer<sup>1</sup> indicates decomposition to occur at 3200 °K.

## 3) Heat of formation

Combustion calorimetry has been used by Humphrey<sup>17</sup> to obtain  $\Delta H_{f,298.15}^\circ = -225.52 \pm 0.23$  kcal gfw<sup>-1</sup>. Mah et al<sup>18</sup> have reported a value of  $-225.8 \pm 0.1$  kcal gfw<sup>-1</sup>, and Ariya et al<sup>19</sup> found  $-224.9 \pm 0.4$  kcal gfw<sup>-1</sup>. These values are all seen to be in excellent agreement. The value selected is based on the work of Mah et al.<sup>18</sup> Probable uncertainty is expected to be about  $\pm 1$  kcal gfw<sup>-1</sup>.



#### 4) Vaporization phenomena

At relatively low temperatures it is expected that stoichiometric  $\text{TiO}_2$  will lose molecular  $\text{O}_2$  to form a compound of the type  $\text{TiO}_{2-x}$ . Brauer and Littke<sup>6</sup> and Assayag et al<sup>20</sup> demonstrated this. Blumenthal and Whitmore,<sup>21</sup> from potential measurements of electrical cells, have measured the relative partial molar free energy of oxygen in the range 850 to 1050°C. They showed that a single-phase region exists from  $\text{TiO}_2$  to  $\text{TiO}_{1.992}$ . The region  $\text{TiO}_{1.992}$  to  $\text{TiO}_{1.968}$  was found to be two-phase. Others who have studied the variation of the relative partial molar free energy of oxygen in the Ti-O system include Kubaschewski and Dench,<sup>22</sup> Komarek and Silver,<sup>23</sup> Hepworth,<sup>24</sup> McClaine,<sup>25</sup> and Mah et al.<sup>18</sup> Kofstad<sup>26</sup> has studied the  $\text{TiO}_{2-x}$  region.

At higher temperatures, gaseous species of  $\text{TiO}$  and  $\text{TiO}_2$  have been observed by Berkowitz et al.<sup>27</sup> A more thorough discussion of vaporization phenomena for the gaseous species  $\text{TiO}$  and  $\text{TiO}_2$  is discussed in their respective sections. Ackermann and Thorn,<sup>28</sup> and Brewer,<sup>1</sup> have discussed the entire system. Vaporization data have been reported by Wheatley and Gilles,<sup>29</sup> and Groves, Hoch, and Johnston.<sup>30</sup>

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#### 30.4.4 Titanium Dioxide (TiO<sub>2(g)</sub>)

##### a. Thermodynamic Functions

In the absence of experimentally derived structural information regarding the TiO<sub>2(g)</sub> molecule, estimates of the appropriate quantities are necessary. Brewer and Rosenblatt<sup>1</sup> assumed this molecule to be linear and used valence bond theory to estimate the vibrational frequencies. Electronic contributions were approximated by use of an ionic model, thus using the energy levels for the Ti<sup>+4</sup> ion.

In the present work, assumptions similar to those of Brewer and Rosenblatt<sup>1</sup> were used. Thus, the molecule is assumed to be linear of the form O-Ti-O. The point group is D<sub>∞h</sub> and the symmetry number is 2. From the vibrational frequency for titanium monoxide, a force constant of  $k_1 = 7.187 \times 10^5$  dyne/cm was calculated. It was assumed that the same stretching force constant was applicable to TiO<sub>2(g)</sub>. The bending force constant  $k_2/l^2$  was assumed to be  $0.034 k_1$  as has been assumed throughout this project. With these force constants, the following vibrational frequencies were estimated:

TABLE 67

##### VIBRATIONAL FREQUENCIES FOR TiO<sub>2(g)</sub>

	cm <sup>-1</sup>	mult
$\omega_1$	873.2	(1)
$\omega_2$	294.1	(2)
$\omega_3$	1127.8	(1)

The interatomic distance in the O-Ti-O molecule was assumed to be 1.620 Å as reported by Sutton<sup>2</sup> for the monoxide. From these data, a moment of inertia  $I = 13.9429 \times 10^{-39}$  gm-cm<sup>2</sup> was computed, and the rotational constant was  $B_e = 0.200739$  cm<sup>-1</sup>.

Electronic energy levels were estimated with the ionic model. Moore<sup>3</sup> lists data for Ti<sup>+4</sup> which show that the ground state has a degeneracy of one and the next higher state is at 436,880 cm<sup>-1</sup>. Hence, higher states do not make any appreciable contribution in the present case.

The uncertainties in structure and electronic contributions for the TiO<sub>2</sub> molecule are considered to lead to appreciable uncertainties in the resultant free energy functions. This is indicated by the estimated uncertainties tabulated in this report. These estimates are generally consistent with the statement by Brewer and Rosenblatt<sup>1</sup> that they feel that the odds are less than 1 in 20 that the free-energy function error exceeds 5 cal deg K<sup>-1</sup> mole<sup>-1</sup>.

b. Heat of Formation

Vaporization data for  $\text{TiO}_2(\text{g})$  over  $\text{TiO}_2(\text{solid})$  have been reported by Berkowitz et al.<sup>4</sup> A third-law analysis of their data using free energy functions for  $\text{TiO}_2(\text{solid})$  and  $\text{TiO}_2(\text{gas})$  from the present work was performed as shown in table 68.

TABLE 68

VAPORIZATION OF  $\text{TiO}_2$  USING THE DATA OF BERKOWITZ et al.<sup>4</sup>  
 ASSUMING THE REACTION  $\text{TiO}_2(\text{solid}) \longrightarrow \text{TiO}_2(\text{gas})$

T (°K)	P <sub>TiO<sub>2</sub></sub> (atm)	$-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)_{\text{TiO}_2(\text{solid})}$	$-\left(\frac{F_T^\circ - H_{298.15}^\circ}{T}\right)_{\text{TiO}_2(\text{gas})}$	$\Delta H_{298.15}^\circ$ (kcal gfw <sup>-1</sup> )
1881	$1.8 \times 10^{-8}$	28.472	69.607	144.036
		(cal deg K <sup>-1</sup> gfw <sup>-1</sup> )		
1881	$2.0 \times 10^{-8}$	28.472	69.607	143.642
1881	$4.0 \times 10^{-8}$	28.472	69.607	141.051
Average $\Delta H_{298.15}^\circ =$				142.910

Using the average heat of sublimation from table 68, and the heat of formation of  $\text{TiO}_2$  accepted on this project of  $-225.8 \text{ kcal gfw}^{-1}$ , the heat of formation of  $\text{TiO}_2(\text{gas})$  is computed as

$$\begin{aligned}\Delta H_f^\circ, \text{TiO}_2(\text{gas}), 298.15 &= 142.910 - 225.8 \\ &= -82.890 \text{ kcal gfw}^{-1}.\end{aligned}$$

This value is accepted in the present work. It is considered subject to an uncertainty of the order of  $\pm 5 \text{ kcal gfw}^{-1}$ .

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### 30. 4. 5 Titanium Sesquioxide ( $\text{Ti}_2\text{O}_3(\text{s}, \ell)$ )

#### a. Crystal Structure, Transition Point, and Melting Point

According to Pearson,<sup>1</sup>  $\text{Ti}_2\text{O}_3$  has a rhombohedral, corundum-type structure. Andersson *et al*<sup>2, 3</sup> have found the phase to have a narrow range of homogeneity, and the lattice parameters have indicated an hexagonal structure with  $a = 5.155 \text{ \AA}$  and  $c = 13.607 \text{ \AA}$ . The limits of the phase have been found to be  $\text{TiO}_{1.49-1.51}$ . Ehrlich<sup>4</sup> has found a much larger homogeneity range of  $\text{TiO}_{1.46}$  to  $\text{TiO}_{1.56}$ .

Naylor<sup>5</sup> has found that  $\text{Ti}_2\text{O}_3$  undergoes a transformation at  $473^\circ \pm 20^\circ\text{K}$ . This is in good agreement with a value of  $475^\circ\text{K}$  reported by Yahia and Frederikse.<sup>6</sup> In the present work, the Naylor value is accepted.

Several melting points have been obtained for  $\text{Ti}_2\text{O}_3$  as shown below.

#### REPORTED MELTING POINTS FOR $\text{Ti}_2\text{O}_3$

Melting Point ( $^\circ\text{K}$ )	Reference
2073	Schofield and Bacon <sup>7</sup>
2093	Brauer and Littke <sup>8</sup>
2193	DeVries and Roy <sup>9</sup>
2173	Junker <sup>10</sup>
2400	Brewer <sup>11</sup>

In the present work, the melting point found by Brauer and Littke<sup>8</sup> at  $2093^\circ\text{K}$  has been accepted.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at $298.15^\circ\text{K}$

Low-temperature heat-capacity data have been obtained by Shomate.<sup>12</sup> The value of  $S_{298.15}^\circ = 18.83 \pm 0.06 \text{ e. u.}$  has been found. A value of  $H_{298.15}^\circ - H_0^\circ = 3.435 \text{ kcal/mole}$ , presumably based on the Shomate data, has been tabulated by JANAF.<sup>13</sup> These data have been accepted in the present work.

## 2) High-temperature heat content

Naylor's<sup>5</sup> data for the range 298° to 1750°K lead to the following equations:

$$C_p^\circ = 7.31 + 53.52 \times 10^{-3} T \text{ cal degK}^{-1} \text{ gfw}^{-1}$$

for 298° to 473°K.

At 473°K, Naylor<sup>5</sup> has found a heat of transition,

$$\Delta H_{473}^\circ = 215 \text{ cal/mole.}$$

Above 473°K, he found a heat-capacity equation of the form:

$$C_p^\circ = 34.68 + 1.30 \times 10^{-3} T - 10.20 \times 10^{-5} T^2 \text{ cal degK}^{-1} \text{ gfw}^{-1}$$

for 473° to 1750°K.

In the present work, this last equation has been extrapolated to the melting point. An estimated heat of fusion of 31.0 kcal/mole by Kubaschewski and Evans<sup>14</sup> has been used at the melting point. The heat capacity of liquid  $\text{Ti}_2\text{O}_3$  has been estimated to be 37.5 cal degK<sup>-1</sup> gfw<sup>-1</sup>. This is consistent with a similar estimate by Glassner.<sup>15</sup>

## 3) Heat of formation

Combustion calorimetry has been performed by Humphrey,<sup>16</sup> Mah et al.,<sup>17,18</sup> and Ariya et al.<sup>19</sup> Heats of formation of  $-362.9 \pm 0.5$ ,  $-363.4$ , and  $-362.8 \pm 0.6$  kcal/mole have been obtained, respectively. It is seen that good agreement resulted.

In the present work, the value  $\Delta H_{f298.15}^\circ = -363.4$  kcal/mole from Mah et al.<sup>17</sup> has been used.

## Supplement

Straumanns and Ejima<sup>20</sup> have reported studies of samples in the vicinity of the  $\text{Ti}_2\text{O}_3$  composition. They have reported hexagonal and rhombohedral lattice parameters as well as other physical properties.



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### 30.4.6 Trititanium Pentoxide ( $\text{Ti}_3\text{O}_5(\text{s}, \theta)$ )

#### a. Crystal Structure, Transition Point, and Melting Point

According to Asbrink and Magneli,<sup>1</sup>  $\text{Ti}_3\text{O}_5$  is dimorphic. At 120°C (393°K), a phase transformation occurs. The high-temperature form is of the anosovite type, whereas the low-temperature form is monoclinic. Naylor<sup>2</sup> has earlier found a transition at 450°K, in general agreement with Asbrink and Magneli.<sup>1</sup> In the present work, the Naylor transformation temperature has been used.

A melting point of approximately 1900°C (2173°K) is obtained from the data of DeVries and Roy.<sup>3</sup> This value is accepted herein.

#### b. Thermodynamic Properties

##### 1) Entropy and heat content at 298.15°K

Experimental low-temperature heat-capacity data by Shomate<sup>4</sup> have yielded  $S_{298.15}^\circ = 30.92 \pm 0.10$  e. u., but the later compilation by Kelley and King<sup>5</sup> tabulates  $S_{298.15}^\circ = 30.9 \pm 0.2$  e. u. A value of  $H_{298.15}^\circ - H_0^\circ = 5.510$  kcal/mole has been tabulated by JANAF,<sup>6</sup> presumably based on the original data from Shomate.<sup>4</sup> In the present work, the values  $S_{298.15}^\circ = 30.9$  e. u. and  $H_{298.15}^\circ - H_0^\circ = 5.510$  kcal/mole are accepted.

##### 2) High-temperature heat content

Naylor<sup>2</sup> has measured the heat content of  $\text{Ti}_3\text{O}_5$  in the range 298° to 1340°K. Kelley<sup>7</sup> has tabulated his results as follows:

$$C_p^\circ = 35.47 + 29.50 \times 10^{-3} T \text{ cal degK}^{-1} \text{ gfw}^{-1}$$

for  $298^\circ\text{K} \leq T \leq 450^\circ\text{K}$ .

At 450°K, the heat of transition is given as

$$\Delta H_{450}^\circ = 2240 \text{ cal/mole.}$$

Above 450°K, the heat-capacity equation is

$$C_p^\circ = 41.60 + 8.00 \times 10^{-3} T \text{ cal degK}^{-1} \text{ gfw}^{-1},$$

valid for the range  $450^\circ\text{K} \leq T \leq 1600^\circ\text{K}$ .

In the present work, the latter equation has been extrapolated to the melting point.

At the melting point, the heat of fusion is estimated to be 50.0 kcal/mole. This is obviously subject to a large uncertainty, perhaps  $\pm 10$  kcal/mole. The heat capacity of liquid  $\text{Ti}_3\text{O}_5$  is estimated to be  $60.0 \text{ cal degK}^{-1}\text{gfw}^{-1}$ .

### 3) Heat of formation

Combustion calorimetry has been used by Humphrey,<sup>8</sup> Mah *et al*,<sup>9</sup> and Ariya *et al*.<sup>10</sup> The data lead to standard heats of formation of  $-586.9 \pm 0.7$ ,  $-587.6$ , and  $-587.0 \pm 1.0$  kcal/mole, respectively. The more recent compilation by Kelley and Mah<sup>11</sup> lists a value of  $\Delta H_f^{298.15} = -587.65$  kcal/mole. This last value, in excellent agreement with the other reported values, is accepted here.

### Supplement

Bright<sup>12</sup> has prepared pure  $\text{Ti}_3\text{O}_5$  in two different crystalline forms, both monoclinic in structure. One form reverts to the other at high temperature. Bright further states that  $\text{Ti}_3\text{O}_5$  exists in two and possibly three crystalline forms. His results are in partial agreement with Asbrink and Magneli,<sup>1</sup> but he does not observe a phase change at  $120^\circ\text{C}$ . Bright indicates that further work is required. A melting point of about  $1710^\circ\text{C}$  ( $1983^\circ\text{K}$ ) is indicated from the work of Brauer and Littke.<sup>13</sup>

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## 31. Tungsten Compounds

The only tungsten compounds investigated in this study were the carbides and oxides.

### 31.1 Tungsten Borides

The borides of tungsten were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 31.2 Tungsten Carbides

In this study, detailed analyses of tungsten carbides were made for  $WC_{(s)}$  and  $W_2C_{(s)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 31.2.1 Tungsten Carbide ( $WC_{(s)}$ and $W_2C_{(s)}$ )

##### a. Phase Diagram, Crystal Structure, and Melting Point

The numerous papers on the carbon-tungsten phase system have been surveyed critically by Hansen and Anderko<sup>1</sup> and Schwarzkopf and Kieffer.<sup>2</sup> The existence of the two phases  $W_2C$  and  $WC$  has been established by the work of many investigators. However, until recently, the phase relations in the carbon-tungsten system have been those established by Sykes,<sup>3</sup> who performed melting-point determinations, microscopic examinations, and qualitative X-ray examinations of alloys with carbon, and Norton,<sup>4</sup> who determined the homogeneity range of  $W_2C$  by X-ray diffraction studies.

A polymorphic transformation of  $W_2C$  has been reported<sup>5-8</sup> to occur at about 2400°C. The crystal structure of the high-temperature  $\beta$ - $W_2C$  has not been fully established.

Melting points for  $W_2C$  of 3153°K by Andrews,<sup>9</sup> 3133°K by Agte and Alterthum,<sup>10</sup> 3023°K by Sykes,<sup>3</sup> 3003°K by Barnes,<sup>11</sup> and 3003°K by Brewer et al.<sup>12</sup> have been reported. Values for  $WC$  of 2923°K by Ruff and Wunsch,<sup>13</sup> 3053°K by Andrews,<sup>9</sup> 3153°K by Friederich and Sittig,<sup>14</sup> 3143°K by Agte and Alterthum,<sup>10</sup> 2873°K by Sykes,<sup>3</sup> 2903°K by Brewer et al.,<sup>12</sup> and 2993°K by Nadler and Kempter.<sup>15</sup> The  $W$ - $W_2C$  eutectic has been placed at about 17.9-atom-percent  $C$  and 2963°K by Ruff and Wunsch,<sup>13</sup> at about 18.9-atom-percent  $C$  and 2748°K by Sykes,<sup>3</sup> and at 3005°K by Nadler and Kempter.<sup>15</sup> Sykes<sup>3</sup> also reported the  $W_2C$  -  $WC$  eutectic to be located at about 41.9-atom-percent  $C$  and 2798°K.

In a comprehensive investigation of the system, Sara and Dolloff<sup>16</sup> have recently shown that the phase diagram is somewhat more complicated.  $W_2C$  has been found to have a broad composition range in the solid state, and incipient melting was observed for compositions between  $W_2C$  and  $W_{2.70}C$ . The maximum melting temperature of  $3068^\circ K$  occurred at a composition of  $W_{2.35}C$ , and the melting was congruent. From differential thermal analysis, metallography, and X-ray studies, no evidence has been found for a high-temperature modification of  $W_2C$  claimed by other investigators.<sup>5-8</sup> A high-temperature modification of WC has been found to exist above  $2798^\circ K$ . In contrast to the lower-temperature hexagonal form, the high-temperature  $\beta$ -WC is fcc with  $a = 4.22 \text{ \AA}$ . This phase is formed by a peritectic reaction at  $3058^\circ K$ . Hexagonal  $\alpha$ -WC is essentially a "line compound" which dissociates at  $3028^\circ K$  into  $\beta$ -WC and graphite. The high-temperature  $\beta$ -WC melts peritectically at  $3058^\circ K$ . The  $W_2C$ ,  $\beta$ -WC eutectic occurs at 36-atom-percent C and  $3033^\circ K$ .

In the table preparation,  $W_2C$  has been assumed to melt at a single temperature with an ideal stoichiometry of  $W_2C$ . The melting temperature of  $3068^\circ K$  reported by Sara and Dolloff has been used. The melting point for monotungsten carbide of  $3058^\circ K$  reported by Sara and Dolloff has been adopted. However because of lack of data on the reported transition from  $\alpha$ -WC to  $\beta$ -WC at  $3028^\circ K$  and because this transition temperature is within 30 deg of the reported melting point, the transition in WC has been neglected. The melting points are probably uncertain by  $\pm 40$  deg.

Both  $W_2C$  and  $\alpha$ -WC are simple hexagonal. Hansen<sup>1</sup> gives, as the most probable values for the lattice constants of  $W_2C$ ,  $a=2.994 \text{ \AA}$  and  $c=4.724 \text{ \AA}$ ; they are in good agreement with the more recent determinations by Nowotny et al.,<sup>17</sup> who found a variation in the "c" parameter across the single-phase region. They obtained  $a=2.99 \text{ \AA}$  and  $c=4.69$  to  $4.72 \text{ \AA}$ , the lower value being obtained at the  $W_2C + W$  phase boundary.

Until recently, the structure of the lower-temperature modification of WC was not completely known. Storms<sup>18</sup> has reviewed the crystallographic data on this compound and, from the results of Parthé,<sup>19</sup> gives  $a=2.90 \text{ \AA}$  and  $c=2.83 \text{ \AA}$ . Parthé assigned the space group  $D_{3h}^{14} P6/m2$ . These values are in very good agreement with the earlier work of Westgren and Phragmen,<sup>20</sup> and Pfau and Rix.<sup>21</sup> In some recent work, Leciejewicz<sup>22</sup> also concluded the space group is  $D_{3h}^{14} P6/m2$  and obtained almost identical values for the lattice parameters.

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\*The term "space group" results from group theory applied to crystallography.

## b. Thermodynamic Properties

### 1) Heat capacity and entropy at 298.15°K

Since no low-temperature heat-capacity data are available for either of the tungsten carbides, the entropies of both carbides are estimated. By comparing  $\Delta S^\circ$  for the reaction,



for a number of transition metal carbides, Krikorian<sup>23</sup> has estimated the entropy of WC at 298.15°K to be  $9.5 \pm 0.5$  e. u., and for  $W_2C$  he estimated  $S_{298.15}^\circ$  to be  $19.5 \pm 1.0$  e. u. These values have been adopted for the table preparation.

### 2) High-temperature heat capacity

No high-temperature heat-content measurements have been made on the tungsten carbides. The high-temperature heat capacities of both carbides have been estimated from the estimated  $S_{298.15}^\circ$  values for this table preparation. The high-temperature heat capacities have been estimated from an equation derived by Krikorian<sup>23</sup> from consideration of the measured high-temperature heat capacities and entropies at 298.15°K for a number of carbides. The equation derived by Krikorian is

$$\begin{aligned} \frac{2 C_p^\circ}{x + y} = & 6.74 + 0.582 S_{298}^\circ \left( \frac{2}{x + y} \right) \\ & + \left[ 2.93 \times 10^{-3} - 0.92 \times 10^{-4} S_{298}^\circ \left( \frac{2}{x + y} \right) \right] T \\ & + \left[ -3.65 \times 10^5 + 1.02 \times 10^4 S_{298}^\circ \left( \frac{2}{x + y} \right) \right] T^{-2}, \end{aligned}$$

in which  $C_p^\circ$  is the heat capacity in cal degK<sup>-1</sup>gfw<sup>-1</sup>, and x and y refer to a carbide of the formula  $M_x C_y$ . The heat-capacity equation obtained for WC is

$$C_p^\circ = 12.27 + 2.06 \times 10^{-3} T - 2.68 \times 10^5 T^{-2} \pm 1.0 \text{ cal degK}^{-1}\text{gfw}^{-1}$$

and for  $W_2C$  the equation obtained is

$$C_p^0 = 21.45 + 2.60 \times 10^{-3} T - 3.48 \times 10^{-5} T^2 \pm 1.4 \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

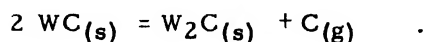
The errors placed on these heat capacities are larger than the errors in the estimated  $S_{298.15}^0$  values for these carbides because they include errors introduced in Krikorian's curve-fitting procedure by which he derived his general equation.

### 3) Heat of formation

The heat of formation of WC has been determined by McGraw and co-workers<sup>24</sup> by combustion calorimetry. The heat of formation of WC determined by this method depends on the value for the heat of formation of  $WO_3$ . Huff, Squitieri, and Snyder<sup>25</sup> subsequently re-determined the heat of formation of  $WO_3$  and corrected the heat of formation of WC determined by McGraw to obtain a standard  $\Delta H_{f298}^0 = -8.4 \pm 0.2 \text{ kcal/mole}$ .

No experimental determinations of the heat of formation of  $W_2C$  have been reported. In this compilation, the estimated value for  $\Delta H_{f298}^0 = -11 \pm 4 \text{ kcal/mole}$  given by Krikorian<sup>26</sup> has been adopted.

Coffman and co-workers<sup>27</sup> have investigated the vaporization behavior of WC. These investigators performed Langmuir weight-loss measurements on hot-pressed samples of WC. They concluded the vaporization proceeds according to



However, the apparent carbon pressures decreased with time during the measurements, probably because of the formation of a layer of  $W_2C$  on the surface of the specimen. Furthermore, because of the high-carbon pressures, polyatomic carbon species should be present in the vapor if equilibrium is achieved in the vapor phase. However, the composition of the vapor above the WC specimens could not be determined. For these reasons, the vaporization experiments have been discontinued. The high apparent vapor pressure of WC does lend support to the rather low heat of formation determined by McGraw.<sup>24</sup>



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### 31.3 Tungsten Nitrides

The nitrides of tungsten were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 31.4 Tungsten Oxides

During the present project, no new investigations of tungsten oxides were made. The earlier study had included analyses for  $\text{WO}_{(g)}$ ,  $\text{WO}_{2(s)}$ ,  $\text{WO}_{2(g)}$ ,  $\text{WO}_{3(s,l)}$ , and  $\text{WO}_{3(g)}$ . Tables for these compounds may be found in section VII (volume 2). For a discussion of these compounds, see Barriault, R. J. *et al.*, Thermodynamics of Certain Refractory Compounds, ASD TR 61-260, Pt. 1, Vol. 1 (May 1962). However, a continued bibliographic search was made, and any reference for such compounds can be found in sections VIII and IX (volume 2).

## 32. Uranium Compounds

The only uranium compounds investigated in this study were the oxides.

### 32.1 Uranium Borides

The borides of uranium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 32.2 Uranium Carbides

The carbides of uranium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 32.3 Uranium Nitrides

The nitrides of uranium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

### 32.4 Uranium Oxides

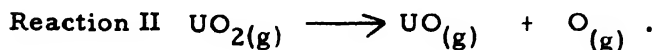
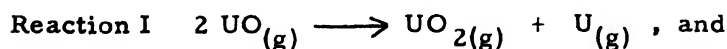
In this study, detailed analyses of uranium oxides were made for  $\text{UO}_{(g)}$ ,  $\text{UO}_{2(s)}$ , and  $\text{UO}_{2(g)}$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 32.4.1 Uranium Monoxide ( $\text{UO}_{(g)}$ )

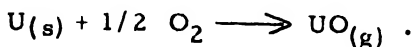
Uranium monoxide does not appear to exist in the condensed phase, but its existence in the vapor phase at high temperatures has been demonstrated mass spectrometrically. Consequently, only the thermodynamic functions for gaseous  $\text{UO}$  have been prepared for the present compilation.

No spectroscopic data are available for  $\text{UO}_{(g)}$ . The vibration frequency and internuclear distance are estimated<sup>1</sup> to be  $920\text{ cm}^{-1}$  and  $1.96\text{ \AA}$ , respectively. The rotational constant  $B_e$  has been calculated to be  $0.2924\text{ cm}^{-1}$ . The ground state has been assumed to be a  $^1\Sigma$  state.

The standard enthalpy of formation  $\Delta H_{f298}^0$  of gaseous  $\text{UO}$  has not been directly determined but could be evaluated from the data of DeMaria et al.<sup>1</sup> These workers measured the equilibria



From the experimental pressures obtained, the equilibrium constant, and thus the standard free-energy change at the experimental temperature, have been computed. The free-energy functions which have already been computed in this program for  $U(g)$ ,  $O(g)$ ,  $UO(g)$ , and  $UO_2(g)$  were then used to determine that  $\Delta H_{f298}^\circ = 22.7 \pm 5$  kcal gfw<sup>-1</sup> for reaction I, and  $165.1 \pm 5$  kcal gfw<sup>-1</sup> for reaction II. The dissociation energy of  $UO$  at 298°K has thus been found to be  $187.8 \pm 10$  kcal gfw<sup>-1</sup>. The enthalpies of formation of  $U(g)$  and  $O(g)$  from the standard states have then been used to obtain  $\Delta H_{f298}^\circ = -11.8 \pm 10$  kcal gfw<sup>-1</sup> for the reaction



It should be noted that the thermodynamic data computed for  $UO$  are based upon estimates of the molecular properties, and upon only one set of experimental data for the equilibrium constant. The computed data should, therefore, be regarded as tentative.

#### REFERENCE FOR SECTION IVB32.4.1

1. DeMaria, G., P. Burns, J. Drowart, and M. Inghram, J. Chem. Phys. 32, 1373 (1960).

#### 32.4.2 Uranium Dioxide ( $UO_{2(s)}$ , $UO_{2(g)}$ )

##### a. Crystal Structure and Melting Point

Stoichiometric  $UO_2$  has a fcc ( $CaF_2$ -type) structure<sup>1</sup> with a lattice parameter of  $a = 5.4704$  Å at 20°C and 5.5246 Å at 946°C.<sup>2</sup> There do not appear to be any phase transitions below the melting point which have been variously reported to be  $2760^\circ \pm 30^\circ C$ ,<sup>3</sup> and  $2878^\circ C$ .<sup>4</sup>

Although  $UO_2$  has been reported to vaporize congruently,<sup>5</sup> this is not true of the many other higher uranium oxides. A thorough review of the properties and stoichiometry of  $UO_2$  and the higher oxides is given by Belle.<sup>6</sup>

##### b. Thermodynamic Properties of $UO_2$ (solid)

###### 1) Heat capacity of the solid

The low-temperature heat-capacity data of Jones, Gordon, and Long,<sup>7</sup> and the high-temperature data of Kelley<sup>8</sup> have been used in this compilation. Popov, Golchenko, and Senin<sup>9</sup> studied the heat capacity of  $UO_2$  over the temperature range of 433° to 876°K and their data are in good agreement with Kelley.

In the preparation of the thermodynamic tables, the tabular heat-capacity data of Jones, Gordon, and Long have been used from 15° to 300°K and the analytical expression,

$$C_p^\circ = 19.20 + 1.62 \times 10^{-3} T - 3.96 \times 10^{-5} T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1},$$

of Kelley has been used from 340° to 3000°K. From 300° to 340°K, the data have been plotted and points have been taken from the smoothed curve. At 15°K,  $S_T^\circ$  has been taken to be 0.12 cal/mole by the Debye extrapolation.

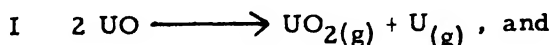
## 2) Heat of formation of the solid

Coughlin's<sup>10</sup> value of  $\Delta H_{f298}^\circ = -259.2 \pm 0.6 \text{ kcal gfw}^{-1}$  has been accepted as the heat of formation of solid  $\text{UO}_2$ .

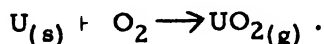
### c. Thermodynamic Properties of $\text{UO}_2$ (gas)

In the absence of experimental spectroscopic data for gaseous  $\text{UO}_2$ , all of the molecular constants required in the calculation of  $C_p^\circ$ ,  $S_T^\circ$ ,  $-(F_T^\circ - H_{298}^\circ)/T$ , and  $H_T^\circ - H_{298}^\circ$  for this report are estimations. The molecular configuration (O-U-O angle = 107 deg, and  $r_{\text{O}} = 1.96 \text{ \AA}$ ) and vibration frequencies (900, 400, and  $925 \text{ cm}^{-1}$ ) have been taken from DeMaria, Burns, Drowart, and Inghram.<sup>11</sup> They are in addition to the assumption of a  $^1\Sigma$  state and the necessary data for uranium and oxygen, the total input data for the computer program.

The standard enthalpy of formation  $\Delta H_{f298}^\circ$  of gaseous  $\text{UO}_2$  has not been directly determined but could be evaluated by two different calculations. The first calculation is based upon the work of DeMaria et al.,<sup>11</sup> for the equilibria



The heats of reaction at 298°K have been evaluated in the same manner as has been described for  $\text{UO}_{(g)}$ , and by utilizing the data for uranium and oxygen already tabulated, a value of  $\Delta H_{f298}^\circ = -117 \pm 10 \text{ kcal gfw}^{-1}$  has been obtained for the reaction



In the second computation, the vapor-pressure data of Ackermann, Gilles, and Thorn<sup>5</sup> for  $\text{UO}_{2(s)} - \text{UO}_{2(g)}$  have been used, along with

the free-energy functions estimated here, to yield  $\Delta H_{298}^{\circ} = 148 \pm 5$  kcal gfw<sup>-1</sup> for the sublimation of UO<sub>2</sub>(s). This, combined with Coughlin's heat of formation of UO<sub>2</sub>(s) yields a heat of formation of UO<sub>2</sub>(g) at 298°K of -111 kcal gfw<sup>-1</sup>.

Since there is some uncertainty about the species obtained by Ackermann et al, the value of  $\Delta H_{f298}^{\circ}$  computed from the data of DeMaria et al is used here.

It should be emphasized that the thermodynamic tables computed here are based upon estimations of the molecular properties of UO<sub>2</sub>(g), and upon only one experimental determination of the equilibrium constants. There is also some doubt about whether UO<sub>2</sub>(s) does vaporize congruently.<sup>12</sup> The gas tables should, therefore, be regarded as tentative.

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### 33. Vanadium Compounds

The only vanadium compounds investigated in this study were the oxides.

#### 33.1 Vanadium Borides

The borides of vanadium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 33.2 Vanadium Carbides

The carbides of vanadium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 33.3 Vanadium Nitrides

The nitrides of vanadium were not investigated; however, a bibliographic search was made, and any references for such compounds can be found in sections VIII and IX (volume 2).

#### 33.4 Vanadium Oxides

In this study, detailed analyses of vanadium oxides were made for  $\text{VO}_2(\text{g})$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

##### 33.4.1 Vanadium Dioxide ( $\text{VO}_2(\text{g})$ )

###### a. Thermodynamic Functions

At the present time, there are no experimental determinations of the structural and spectroscopic properties of  $\text{VO}_2$  (gas). Brewer and Rosenblatt<sup>1</sup> have noted that it may be at least 10 years or more before such data become available. In the meantime, it is desirable to estimate these properties.

Brewer and Rosenblatt<sup>1</sup> have estimated data for  $\text{VO}_2(\text{g})$  in the following way. They assume it to be a linear molecule with interatomic distances equal to those of the monoxide. Valence bond theory was used to estimate the vibrational frequencies. An ionic model was used to estimate the electronic contributions.

In the present work, a procedure analogous to that of Brewer and Rosenblatt<sup>1</sup> was used. It was assumed that the molecule is linear

O-V-O with a  $D_{\infty h}$  symmetry (symmetry number = 2). The interatomic O-V distance was assumed to be 1.59 Å as tabulated by Sutton<sup>2</sup> for the monoxide. A moment of inertia  $I = 13.4312 \times 10^{-39}$  gm cm<sup>2</sup> and a rotational constant  $B_e = 0.20838$  cm<sup>-1</sup> were calculated.

From the vibrational frequency (1012.3 cm<sup>-1</sup>) for the monoxide, a stretching force constant  $k_1 = 7.350 \times 10^5$  dyne/cm was calculated which was assumed applicable to the dioxide. The bending force constant was assumed to be 0.034  $k_1$ , as has been assumed for other triatomic gases. From the above data, the valence bond theory has been used to calculate the following frequencies:

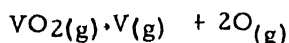
$$\omega_1 = 883.1 \text{ cm}^{-1} (1) \quad (\text{multiplicity} = 1)$$

$$\omega_2 = 293.8 \text{ cm}^{-1} (2) \quad (\text{multiplicity} = 2)$$

$$\omega_3 = 1126.8 \text{ cm}^{-1} (1) \quad (\text{multiplicity} = 1).$$

#### b. Heat of Formation

Brewer and Rosenblatt<sup>1</sup> analyzed the data of Berkowitz, Chupka, and Inghram.<sup>3</sup> They derived a heat of dissociation for VO<sub>2</sub>(g), at 298.15°K, of  $\Delta H_{298}^\circ = 298 \pm 10$  kcal/mole. Converting this to a heat of formation for VO<sub>2</sub>(g) using data for V(g) and O(g) from the present project, the following is obtained:



$$\Delta H_{f; \text{VO}_2(\text{g}); 298}^\circ = \Delta H_{\text{sub}; \text{V}(\text{g}); 298}^\circ + 2 \Delta H_{f; \text{O}(\text{g}); 298}^\circ - \Delta H_{\text{diss}; \text{VO}_2(\text{g}); 298}^\circ$$

$$= 123.010 + 2 (59.557) - 298$$

$$\Delta H_{f; \text{VO}_2(\text{g}); 298}^\circ = -55.876 \text{ kcal/mole.}$$

This value for the heat of formation of VO<sub>2</sub>(g) is not to be considered a final value since it was not derived using internally self-consistent functions. However, it is likely that a recalculation will not change the derived heat of formation more than the uncertainty of  $\pm 10$  kcal/mole. The present value is accepted for the heat of formation; i.e.,  $\Delta H_{f298.15}^\circ = -55.876 \pm 10$  kcal/mole, although it is subject to revision.



#### REFERENCES FOR SECTION IVB33.4.1

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2. Sutton, L. E. , Tables of Interatomic Distances and Configurations in Molecules and Ions, Special Publication No. 11, The Chemical Society, London (1958).
3. Berkowitz, J. , W.A. Chupka, and M.G. Inghram, J. Chem. Phys. 27, 87 (1957).

## 34. Yttrium Compounds

Selected borides, carbides, nitrides, and oxides of yttrium were investigated.

### 34.1 Yttrium Borides

Three borides are mentioned in the literature; i. e.,  $YB_4$ ,  $YB_6$ , and  $YB_{12}$ . Of these, only the second has been well described.<sup>1,2</sup> The structure is of the  $CaB_6$  type, the metal atoms forming a simple cubic lattice and the boron atoms forming octahedral  $B_6$  groups in the center of the unit cell. The lattice distance reported by Tvorogov<sup>1</sup> is  $a_0 = 4.126 \text{ \AA}$ ; Kiessling<sup>3</sup> reported  $4.08 \text{ \AA}$ . The melting point is approximately  $2300^\circ\text{C}$ .<sup>2</sup>

For a review of the other borides, see Binder<sup>4</sup> and Samsonov.<sup>5</sup>

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### 34.2 Yttrium Carbides

Four carbides are mentioned in the literature, i. e.,  $YC$ ,  $YC_2$ ,  $Y_2C_3$ , and  $Y_3C$ ; the most important is  $YC_2$ .

Yttrium dicarbide has the body-centered tetragonal structure of  $CaC_2$  type;  $a = 3.664 \text{ \AA}$  and  $c = 6.169 \text{ \AA}$ .<sup>1,2</sup> No thermodynamic data are available.

For the sesquicarbide, neither structural nor thermodynamic information is available.

The "trityttrium carbide" refers to material of somewhat variable composition.<sup>1</sup> It is stated to be face-centered cubic.

The monocarbide has been prepared by Samsonov et al.;<sup>3</sup> it is unstable in air, decomposes in water, and melts at  $1950^\circ \pm 20^\circ\text{C}$ .

## Supplement

DeMaria and Guido<sup>4</sup> have made a thermodynamic study of the Y-C system.

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### 34. 3 Yttrium Nitrides

YN has the NaCl structure, the lattice constant being 4.877 Å at 23°C.<sup>1</sup> The melting point is stated<sup>1</sup> to be 2670°C in the presence of N<sub>2</sub> at a pressure of 1 atm. The heat of formation is estimated by Huber et al<sup>2</sup> to be -75 kcal/gfw, while Kubaschewski and Evans<sup>3</sup> give the value  $-71.5 \pm 5$  kcal/gfw; the latter estimate  $S_{298}^0 = 11.0$  eu.

### REFERENCES FOR SECTION IVB34. 3

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2. Huber, E. J., E. L. Head, and C. E. Holley, J. Phys. Chem. 61, 497 (1957).
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### 34. 4 Yttrium Oxides

In this study, detailed analyses of yttrium oxides were made for  $\text{YO}_{(g)}$  and  $\text{Y}_2\text{O}_{3(s)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 34. 4. 1 Yttrium Monoxide ( $\text{YO}_{(g)}$ )

Yttrium monoxide does not appear to exist as a condensed phase, and hence present calculations are for the ideal gas. The spectroscopic constants  $\omega_e$  and  $\omega_e x_e$  were taken from Herzberg,<sup>1</sup>  $\omega_{ey_e}$  for the  $X^2\Sigma$  state was taken from Rosen,<sup>2</sup> values of  $E = \nu_{00}$  were taken from the recent work of Uhler and Akerlind.<sup>3, 4</sup> The constants  $B_0$  and  $D_0$  given in the two papers of Uhler and Akerlind are essentially the same, however, those of the second paper have been used herein. The rotational constants  $a_e$  were calculated from Pekeris' equation<sup>5</sup> and are in agreement with those calculated by Uhler and Akerlind. The rotational constants  $B_e$  were calculated from the equation<sup>1</sup>

$$B_e = B_0 + a_e/2, \quad (\text{IVB34. 4. 1-1})$$

but they are not in accord with those given by Uhler and Akerlind which apparently are calculated from

$$B_e = B_0 - a_e/2. \text{ Values of } D_e \text{ were calculated from } D_e = \frac{4B_e^3}{\omega_e^2}$$

and are numerically the same as the  $D_0$  values of Uhler and Akerlind. The spectroscopic constants are summarized in table 69.

Thermochemical data have been calculated for YO gas using the diatomic gas program. Previous calculations of this general type have been performed by Kelley and King<sup>6</sup>. At 298.15°K, they find  $S_{298}^\circ = 56.3 \pm 0.5$  made up of the following contributions:

$$S_{\text{trans}}^\circ = 39.86, S_{\text{rot}}^\circ = 14.91, S_{\text{vib}}^\circ = 0.17, \text{ and } S_{\text{elec}}^\circ = 1.38 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}.$$

For the dissociation energy  $D_0^\circ$ , Ga,<sup>7</sup> gives  $7 \pm 2 \text{ ev}(161 \pm 46 \text{ kcal gfw}^{-1})$  while Herzberg<sup>1</sup> gives  $9 \pm 2 \text{ ev}(207 \pm 46 \text{ kcal gfw}^{-1})$ . The lower value is quoted by Brewer<sup>8</sup>. From a study of the vaporization of  $\text{Y}_2\text{O}_3$  by a Knudsen effusion technique, Walsh, Goldstein, and White<sup>9</sup> conclude that, for the reaction

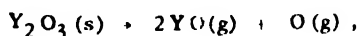
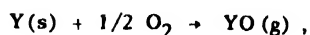


TABLE 69

SPECTROSCOPIC CONSTANTS FOR YO  
(All Values in  $\text{cm}^{-1}$ )

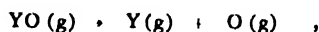
State Constant	$X^2\Sigma$	$A^2\pi$	$A^2\pi$	$B^2\Sigma$
E	0	16294.72	16722.75	20741.92
$\omega_e$	852.5	812.7	808.9	765.03
$\omega_e x_e$	2.45	2.80	2.96	7.75
$\omega_e y_e$	0.0273	0	0	0
$B_0$	0.3881	0.3857	0.3857	0.3722
$B_e$	0.3889	0.3867	0.3867	0.3742
$a_e$	0.0016	0.0019	0.0019	0.0039
$\gamma_e$	0	0	0	0
$D \times 10^7$	3.2	3.5	3.5	3.9
$g$	2	2	2	2

$\Delta H_0^\circ = 489 \text{ kcal/gfw}$ . By use of a cycle involving data quoted in this report, it is found that, for the reaction



$\Delta H_0^\circ = -11.8 \text{ kcal/gfw}$ . This agrees exactly with the value given by Walsh et al<sup>9</sup> who quote a precision measure of  $\pm 4 \text{ kcal/gfw}$ , presumably determined essentially by the uncertainty of  $\Delta H_0^\circ$  for the dissociation of  $\text{Y}_2\text{O}_3$ .

Finally, for the reaction



making use of  $\Delta H_0^\circ (\text{sub}) = 101.3 \text{ kcal/gfw}$ ,  $D_0^\circ = 172.1 \pm 5 \text{ kcal/gfw}$ , or  $7.46 \pm 0.2 \text{ ev}$ , is calculated, which replaces Walsh's value of  $7 \pm 0.2 \text{ ev}$ .

Brewer and Chandrasekhariah<sup>10</sup> have calculated the free-energy function (fef) of YO at a series of temperatures from 298° to 3000°K. They estimate the electronic contribution by assuming that molecular states may be approximated by the energy levels of the corresponding +2 metal ions, and that the approach of an oxide ion causes no drastic perturbations. Electronic partition functions for the oxides are then calculated from the energy levels of the corresponding +2 cations taken from Moore's tables.

A selection of their data follows:

TABLE 70  
DATA FOR YO(g)

<div style="text-align: center;">T(°K)</div> Function	298	1000	1500	2000	2500	3000
-(fef) elect	2.8	3.6	3.9	4.0	4.1	4.2
-(fef) rot	12.44	14.84	15.65	16.22	16.66	17.02
-(fef) vib	0.03	0.69	1.16	1.55	1.88	2.17
-(fef) trans	34.89	40.91	42.92	44.35	45.46	46.36
-(fef)tot	50.16	60.05	63.63	66.17	68.10	69.76

Kelley<sup>11</sup> has made a calculation of the type given here.

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### 34. 4. 2 Yttrium Sesquioxide ( $Y_2O_3(s)$ )

#### a. Crystal Structure, Melting Point, Boiling Point

$Y_2O_3$  has the  $Tl_2O_3$  bcc structure with many oxygen positions vacant.<sup>1</sup> The unit cell length is  $a_0 = 10.604 \text{ \AA}$ ; the density is  $4.64 \text{ gm/cm}^3$ . According to Curtis,<sup>2</sup> and Stecura and Campbell,<sup>3</sup> the structure is stable up to  $1800^\circ\text{C}$  and no phase inversion occurs. At  $80^\circ\text{C}$ , the coefficient of thermal expansion<sup>3</sup> is  $7.0 \times 10^{-6}$  and at  $1300^\circ\text{C}$  it is  $8.9 \times 10^{-6}$ .

There have been no recent determinations of the melting point. Ruff and Laushke<sup>4</sup> give the melting point as  $2410^\circ\text{C}$ , a value which is quoted by the ICT.<sup>5</sup> According to Kubaschewski and Evans,<sup>6</sup> the melting point is given as  $2420^\circ\text{C}$  with no citation of source, and Cassedanne and Forestier<sup>7</sup> adopt approximately the same value in their phase diagram of the  $La_2O_3 - Y_2O_3$  system. In his critical review, Brewer<sup>8</sup> gave the melting point as  $2690^\circ \pm 100^\circ\text{K}$ .

The boiling point has been estimated by Brewer<sup>8</sup> as  $4570^\circ \pm 300^\circ\text{K}$ ; the same value is given by Kubaschewski and Evans.<sup>6</sup> Presumably, they are here following Mott,<sup>9</sup> who gives the boiling point as  $4300^\circ$  to  $4600^\circ\text{C}$ , and Richardson,<sup>10</sup> who estimates the boiling point as  $4600^\circ\text{C}$ . A modern re-determination is required.

#### b. Heat of Formation

The heat of formation of  $\text{Y}_2\text{O}_3$  as determined by direct combustion of the metal<sup>11</sup> is

$$\Delta H_{f,298.15}^\circ = -455.45 \pm 0.54 \text{ kcal/gfw} \quad (\text{IVB34.4.2-1})$$

#### c. Heat Capacity, Enthalpy, and Entropy

The heat capacity from  $15^\circ$  to  $299^\circ\text{K}$  has been measured by Goldstein *et al*<sup>12</sup>. At  $298.15^\circ\text{K}$ ,  $C_p^\circ = 24.50 \text{ cal/gfw }^\circ\text{K}$ ,  $S^\circ = 23.693 \pm 0.07 \text{ cal/gfw }^\circ\text{K}$ ,  $(H_{298}^\circ - H_0^\circ) = 3989.3 \text{ cal/gfw}$ , and  $-(F_T^\circ - H_0^\circ)/T = 10.313 \text{ cal/gfw }^\circ\text{K}$ . The Debye temperature is estimated as  $178$ . On the assumption that the temperature dependence of the high-temperature heat capacity is the same as that of  $\text{La}_2\text{O}_3$  as determined by Blomeke and Ziegler,<sup>13</sup> Goldstein *et al*<sup>12</sup> estimate the entropies, enthalpies, and free-energy functions given in table 71.

TABLE 71  
THERMODYNAMIC FUNCTIONS OF  $\text{Y}_2\text{O}_3(\text{s})$

T	$S^\circ$	$(H_T^\circ - H_0^\circ)$	$-(F_T^\circ - H_0^\circ)/T$
$^\circ\text{K}$	$\text{cal } ^\circ\text{K}^{-1} \text{ gfw}^{-1}$	$\text{cal gfw}^{-1}$	$\text{cal } ^\circ\text{K}^{-1} \text{ gfw}^{-1}$
298.15	23.69	3989	10.31
500	37.98	9615	18.75
1000	59.08	24930	34.15
1500	72.18	41130	44.76
2000	82.00	58220	52.89
2500	89.97	76125	59.52



The assumption of Goldstein et al<sup>12</sup> appears to be in good agreement with the statement of Curtis and Tharp<sup>14</sup> who report an average molar heat capacity between 0° and 100°C of 29.86 cal/°K gfw.

A thermodynamic table was not prepared.

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## 35. Zirconium Compounds

Selected borides, carbides, nitrides, and oxides of zirconium were investigated.

### 35.1 Zirconium Borides

In this study, detailed analyses of zirconium borides were made for  $\text{ZrB}_2(\text{s}, \ell)$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

#### 35.1.1 Zirconium Diboride ( $\text{ZrB}_2(\text{s}, \ell)$ )

In the zirconium-boron system, the diboride  $\text{ZrB}_2$  is very refractory. It is one of the few borides whose thermodynamic properties have been even moderately investigated. However, recent years have seen several investigations of this potentially useful refractory material. One of the big problems hampering thorough investigations has been the obtaining of pure, well characterized specimens. Several reviews with data on these and other borides have been published by Samsonov and Markovski<sup>1</sup> and Aronsson.<sup>2, 3</sup>

##### a. Phase Data, Crystal Structure, and Melting Point

A phase diagram given by Hansen and Anderko<sup>4</sup> is based on the work of Glaser and Post.<sup>5</sup> Leitnaker<sup>6</sup> and Leitnaker *et al*<sup>7</sup> have utilized the same diagram with only minor modifications. According to this diagram,  $\text{ZrB}_2$  is the dominant phase with a melting point of  $3040^\circ\text{C}$  ( $3313^\circ\text{K}$ ). This phase is shown to have a very limited range of homogeneity. A "ZrB" phase is shown to be stable between  $800^\circ$  and  $1250^\circ\text{C}$  ( $1073^\circ$  to  $1523^\circ\text{K}$ ). The  $\text{ZrB}_{12}$  phase is shown to exist between  $1700^\circ$  and  $2680^\circ\text{C}$  ( $1973^\circ$  to  $2953^\circ\text{K}$ ). Aronsson<sup>3</sup> (p. 162) shows the same diagram but omits the "ZrB" phase. He contends that, in cases where this phase has been observed, considerable O, C, or N might have been present to give the cubic structure which has been ascribed to the "ZrB" phase.

Nowotny, Rudy, and Benesovsky<sup>8</sup> studied the ternary Zr-B-C system at  $1400^\circ\text{C}$  ( $1673^\circ\text{K}$ ). They did not observe either the ZrB or  $\text{ZrB}_{12}$  phase. Their results at  $1400^\circ\text{C}$  appear compatible with the Glaser and Post<sup>5</sup> diagram or the Aronsson<sup>3</sup> interpretation. Koval'chenko, Samsonov, and Yasinskaya<sup>9</sup> have obtained hypothetical phase diagrams for the  $\text{ZrB}_2$ -Cr and  $\text{ZrB}_2$ -Mo systems.

Rudy and Benesovsky<sup>10</sup> have reported studies for the binary Zr-B system and the ternary Zr-B-N system. For the Zr-B system with studies of hot-pressed samples in the region 40- to 60-atom-percent boron, they found very small amounts of the cubic "ZrB" phase in addition to

ZrB<sub>2</sub> and Zr. Lattice constants of this cubic "ZrB" phase varied between 4.65 and 4.68 Å in agreement with literature data. For some specimens they could not find the cubic phase, but only ZrB<sub>2</sub>. For melted samples (30- to 60-atom-percent B), they found only very small amounts of the "ZrB" cubic (B1) phase. In addition, they could not find X-ray lines for the B27-type structure. In the ZrB<sub>2</sub> phase (C32 type), they found  $a = 3.167 \text{ Å}$  and  $c = 3.530 \text{ Å}$ , in agreement with other published data. For compositions of 60- to 75-atom-percent boron, they found no appreciable homogeneity range. For compositions with higher boron contents, the ZrB<sub>12</sub> cubic phase with  $a = 7.408 \text{ Å}$  occurs. This phase is not stable below 1800°C.

In the ternary Zr-B-N section at 1500°C, Rudy and Benesovsky<sup>10</sup> observed ZrN, ZrB<sub>2</sub>, and Zr(N,B)<sub>1-x</sub> phases.

From this review of the phase data, there is general agreement that ZrB<sub>2</sub> is the most refractory phase. The data on "ZrB" are still uncertain; however, in any event, it is not of as much interest as the diborides.

Zirconium diboride has a narrow homogeneity range and is of the hexagonal AlB<sub>2</sub> (C32) type structure, according to the phase data summarized by Hansen and Anderko.<sup>4</sup> From Aronsson,<sup>2</sup> the lattice parameters are listed as  $a = 3.170 \text{ Å}$  and  $c = 3.533 \text{ Å}$ . In earlier work,<sup>3</sup> Aronsson gives  $a = 3.169 \text{ Å}$  and  $c = 3.530 \text{ Å}$ , based primarily on the works of Kiessling<sup>11</sup> and Epel'baum and Gurevich.<sup>12</sup> Aronsson points out that constancy of lattice parameters as composition varies indicates a narrow homogeneity range.

An attempt to melt ZrB<sub>2</sub> in an electron-beam apparatus was unsuccessful in the work of Martin *et al.*<sup>13</sup> Excessive vaporization under the low-pressure conditions prevented successful melting. More conventional methods of obtaining melting-point data have been summarized by Hansen and Anderko.<sup>4</sup> Values of 3313°K, based on the work of Glaser and Post,<sup>5</sup> and 3273°K, via the work of Moers,<sup>14</sup> were reported. For the present tabulation, the value of 3313°K was accepted.

## b. Thermodynamic Properties

### 1) Heat of fusion

Because of the high melting temperature, there were no experimental determinations available for the heat of fusion of ZrB<sub>2</sub>. For the present case, it was necessary to estimate this quantity. The assumption was made that the entropy of melting is  $2.6 \text{ cal}^\circ\text{K}^{-1} \text{ g atom}^{-1}$ , based on a procedure from Kubaschewski and Evans<sup>15</sup> (p. 192). Thus, a calculated value of 25,841 cal/mole was rounded

off to 25,000 cal/mole. This accepted value of 25,000 cal/mole for the heat of fusion of  $\text{ZrB}_2$  at 3313°K is clearly subject to a large uncertainty. It is felt likely to be as large as  $\pm 5000$  cal/mole. The only other value estimated for the heat of fusion of  $\text{ZrB}_2$  is a value of  $\Delta H^\circ = 13,000 \pm 3000$  cal/mole from the JANAF<sup>16</sup> tables. This value was estimated by addition of the heats of melting of the component elements.

## 2) Entropy and heat content at 298.15°K

The only low-temperature heat-capacity data for  $\text{ZrB}_2$  are those of Westrum.<sup>17</sup> The specimen used had been zone-refined and showed an analysis very close to stoichiometric. Thus, the results should be quite reliable. At 298.15°K, it was found that  $S_{298.15}^\circ = 8.586$  e. u.,  $C_p^\circ = 11.53$  cal/mole °K, and  $H_{298}^\circ - H_0^\circ = 1590$  cal/mole. These data were accepted for the present tabulation.

## 3) High-temperature heat content

In recent years, there have been several investigations of the high-temperature heat capacity of  $\text{ZrB}_2$ .<sup>18-26</sup> Unfortunately, the agreement between the different works is not good. Mezaki et al<sup>18</sup> have measured heat contents of  $\text{ZrB}_2$  over the range 429° to 1171°K, using a drop technique. These data were smoothed to give a table of  $C_p^\circ$  and heat contents from 298.15° to 1200°K. The same data had also been published in a separate report.<sup>20</sup> The  $\text{ZrB}_2$  specimen used for these studies had been obtained from the Carborundum Company. Gold capsules were used as containers.

The derived data published<sup>18, 20</sup> gave a heat-capacity equation of the form

$$C_p^\circ = 15.81 + 4.20 \times 10^{-3}T - 3.52 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1} \quad (\text{IVB35.1.1-1})$$

This led to a value of

$$C_{p, 298.15}^\circ = 13.16 \text{ cal/mole }^\circ\text{K} \quad (\text{IVB35.1.1-2})$$

Such a value is at variance with the low-temperature result of Westrum;<sup>17</sup> i. e.,

$$C_{p, 298.15}^\circ = 11.53 \text{ cal/mole }^\circ\text{K} \quad (\text{IVB35.1.1-3})$$

More recent work by Margrave<sup>19</sup> has utilized a zone-refined specimen of  $\text{ZrB}_2$  studied in gold and platinum capsules. Experimental data were tabulated for  $\text{ZrB}_2$  samples from 410° to 773°K and 336° to 1125°K. Smoothed data had not yet been obtained.

Neel et al<sup>21</sup> measured the heat capacity of a specimen of  $\text{ZrB}_2$  from the Norton Company, which showed a composition close to that of  $\text{ZrB}_2$  (although the report lists  $\text{ZrB}$ ). For the temperature range  $533^\circ \leq T \leq 2477^\circ\text{K}$ , they found a heat-capacity relation which can be reduced to

$$C_p^\circ = 3.457 + 23.228 \times 10^{-3}T - 6.332 \times 10^{-6}T^2 \text{ cal/mole } ^\circ\text{K} \quad .$$

(IVB35.1.1-4)

Prophet<sup>22-24</sup> obtained data for  $\text{ZrB}_2$  for the range 1300° to 2150°K, via a rate-of-cooling method.

Ihnat<sup>25</sup> used a pulse technique to measure the heat capacity of  $\text{ZrB}_2$  for a temperature range of 1739° to 2521°K. The investigation indicated excessive specific heats. Thus at 2521°K, a molar heat capacity of 43.9 cal/mole °K was found. This value is almost double that predicted on the basis of simple Debye lattice theory and has not been confirmed.

Earlier work had been reported by Krestovnikov and Vendrikh.<sup>26</sup> They found a relation for the heat capacity in the temperature range 273° to 1073°K of the form

$$C_p^\circ = 11.78 + 9.986 \times 10^{-3}T - 4.028 \times 10^{-6}T^2 \text{ cal/mole } ^\circ\text{K} \quad .$$

(IVB35.1.1-5)

Various methods of treating the high-temperature heat-capacity data have been tried and are summarized in table 72. The accompanying legend describes the manner of calculations. In the case of legend 3, an equation was derived by the Shomate method based on the enthalpy contents of Margrave and Prophet's<sup>22</sup> data as tabulated by JANAF. Subsequently, Prophet<sup>24</sup> has informed Avco RAD that his basic data are not enthalpy content but heat capacity. Therefore, the treatment is not exactly correct although it gives a reasonable interpretation of the data. It is included here only to illustrate the data obtained with this particular equation.

For the present analysis, a choice of data has been obtained by using a Shomate function to join the Westrum data<sup>17</sup> with the Margrave<sup>19</sup> and Neel et al<sup>21</sup> data. As seen in table 72, this treatment (legend 9) gives a much more realistic heat capacity at high temperatures than the original equation from Neel et al.<sup>21</sup>

TABLE 72  
COMPARISON OF  $ZrB_2$  CALCULATIONS

Temperature	Source (See Legend)	$C_p^\circ$	$S_T^\circ$	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298.15}^\circ$
$^\circ K$		$cal^\circ K^{-1} gfw^{-1}$			$kcal\ gfw^{-1}$
298.15	1	13.482	8.586	8.586	0.0
	2	12.878	8.586	8.586	0.0
	3	11.531	8.586	8.586	0.0
	4	14.399	8.586	8.586	0.0
	5	13.102	8.586	8.586	0.0
	6	9.820	8.586	8.586	0.0
	7	11.53	8.59	8.59	0.0
	8	---	---	---	---
	9	11.53	8.59	8.59	0.0
1000	1	18.798	26.760	15.834	10.926
	2	18.820	26.685	15.788	10.897
	3	19.645	27.378	15.941	11.436
	4	17.738	28.015	16.506	11.510
	5	19.658	28.862	16.682	12.181
	6	20.353	26.188	15.234	10.953
	7	19.750	28.002	16.182	11.819
	8	---	---	---	---
	9	18.970	27.624	16.108	11.516
2000	1	29.233	42.973	25.515	34.915
	2	33.970	43.933	25.614	36.638
	3	27.672	43.480	25.917	35.127
	4	15.640	40.125	25.690	28.870
	5	24.122	43.889	26.832	34.115
	6	24.585	42.314	25.075	34.477
	7	22.945	42.834	26.136	33.397
	8	38.	---	---	---
	9	23.784	42.287	25.815	32.945
2500	1	34.509	50.063	29.722	50.850
	2	44.491	52.607	30.138	56.172
	3	31.613	50.079	30.099	49.949
	4	11.570	43.215	28.912	35.757
	5	26.254	49.501	30.817	46.710
	6	21.952	47.576	29.078	46.244
	7	23.953	48.067	30.014	45.133
	8	42.	---	---	---
	9	26.071	47.840	29.677	45.409
3000	1	39.79	56.821	33.679	69.426
	2	56.975	61.792	34.640	81.456
	3	35.544	56.190	33.944	66.738
	4	5.486	44.817	31.449	40.105
	5	28.371	54.475	34.353	60.366
	6	16.153	51.113	32.479	55.902
	7	24.700	52.504	33.402	57.307
	8	---	---	---	---
	9	28.342	52.795	33.123	59.013

# LEGEND TO TABLE 72

1. Margrave's<sup>19</sup> enthalpy data are fitted by least squares to give  $C_p^\circ = 8.001 + 0.01059T + 2.0654 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .
2. Margrave's<sup>19</sup> enthalpy data are fitted by least squares to give  $C_p^\circ = 11.524 + 0.003369T + 3.927 \times 10^{-6}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .
3. Margrave's<sup>19</sup> and Prophet's<sup>22</sup> enthalpy data fitted to Westrum's<sup>17</sup> low-temperature data using Shomate function to give  $C_p^\circ = 12.064 + 7.836 \times 10^{-3}T - 2.551 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .
4. Krestovnikov and Vendrikh<sup>26</sup> using their equation to give  $C_p^\circ = 11.78 + 9.986 \times 10^{-3}T - 4.028 \times 10^{-6}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .
5. Margrave's et al<sup>19, 20</sup> data using their published equation <sup>20</sup> to give  $C_p^\circ = 15.81 + 4.20 \times 10^{-3}T - 3.52 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .
6. Neel et al<sup>21</sup> gave an equation which reduces to  $C_p^\circ = 3.457 + 23.228 \times 10^{-3}T - 6.332 \times 10^{-6}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .
7. JANAF data.<sup>16</sup>
8. Ihnat.<sup>25</sup>
9. Present calculations using Shomate function with Margrave<sup>19</sup> and Southern Research Institute data<sup>21</sup> to give  $C_p^\circ = 14.888 + 4.50 \times 10^{-3}T - 4.178 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$ .

Also, the present treatment gives free-energy functions in good agreement with those tabulated by JANAF.<sup>16</sup> The equation adopted is

$$C_p^\circ = 14.888 + 4.50 \times 10^{-3}T - 4.178 \times 10^{-5}T^2 \text{ cal}^\circ\text{K}^{-1} \text{ gfw}^{-1}.$$

(IVB35.1.1-6)

This equation has been extrapolated to the melting point.

Beyond the melting point, the heat capacity for the liquid phase was assumed constant and equal to the value of the solid at the melting point.

#### 4) Heat of formation

Three independent calorimetric determinations have been performed on zirconium diboride. Recently, Hubbard's laboratory at Argonne National Laboratories has used fluorine combustion to obtain  $\Delta H_{f298, \text{ZrB}_2}^\circ = -71.5 \text{ kcal gfw}^{-1}$ .<sup>27, 28</sup> Earlier Huber et al<sup>29</sup> had used oxygen-bomb calorimetry to obtain  $\Delta H_{f298, \text{ZrB}_2}^\circ = -76.7 \text{ kcal gfw}^{-1}$ , while Epel'baum and Starostina<sup>30</sup> by a similar method obtained  $\Delta H_{f298, \text{ZrB}_2}^\circ = -75.02 \pm 3.35 \text{ kcal gfw}^{-1}$ . This last work used questionable data for the combustion of boron as remarked by Westrum and Feick<sup>17</sup> and others.

It is possible that Epel'baum and Starostina<sup>30</sup> may have made simultaneous errors the net effect of which is to cancel each other out, giving a correct heat of formation. The general agreement between these three determinations appears relatively good.

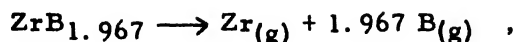
For the present analysis, it is felt advisable to give the greatest weight to the fluorine bomb calorimetric results. Accordingly, a value of  $-73 \text{ kcal/gfw}$  is selected as the heat of formation for  $\text{ZrB}_2$ . Until further details become available, it is suggested that the uncertainty is  $\pm 2 \text{ kcal/gfw}$ .

Vaporization experiments from  $\text{ZrB}_2$  can also be used to derive heat-of-formation data. Such experiments have been performed by Leitnaker et al,<sup>6, 7</sup> Goldstein and Trulson,<sup>31</sup> Bolgar et al,<sup>32</sup> and Buchler.<sup>33</sup> In addition, Kibler, Lyon, and DeSantis<sup>34</sup> have discussed the possibility of vaporizing boron from a  $\text{ZrB}_2$  cell as had been reported earlier by Searcy and Myers.<sup>35</sup>

The vaporization studies of Leitnaker et al<sup>6, 7</sup> and Goldstein and Trulson<sup>31</sup> appear to be the most thorough. Leitnaker et al<sup>6, 7</sup> originally reported that vaporization occurs congruently for a composition of  $\text{ZrB}_{1.906}$ . Later analyses reported by Leitnaker<sup>36</sup> indicate that the congruent vaporization occurred at  $\text{ZrB}_{1.967}$ . This is in good agreement with a value of  $\text{ZrB}_{1.96}$  found by Buchler.<sup>33</sup> On the other hand, Goldstein and Trulson<sup>31</sup> do not indicate vaporization at other than the stoichiometric  $\text{ZrB}_2$ . Bolgar et al<sup>32</sup> reported no composition change when  $\text{ZrB}_2$  vaporizes in a vacuum at  $1700^\circ\text{C}$ .



Leitnaker<sup>36</sup> has indicated that re-calculation of his data for the equilibria



using free-energy functions from Margrave, 19, 20 give

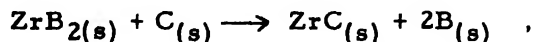
$$\Delta H_0^\circ = 474.8 \text{ kcal/gfw.}$$

It is of interest to compare this value with computations using data already presented in this report for heat of sublimation of Zr and B, and the value of - 73 kcal/gfw for the heat of formation of  $\text{ZrB}_2$ .

Sublimation	kcal/gfw
Sublimation of Zr at 0°K	142.810
Sublimation of B at 0°K = 1.967 x 131.779	259.209
$\Delta H_f^\circ, \text{ZrB}_{1.967}$ estimated as $\frac{1.967}{2} \times 73$	71.759
Total Heat of Sublimation of $\text{ZrB}_{1.967}$	473.778

It is seen that very good agreement results. Obviously, it would be better to use internally consistent free-energy functions and re-compute the original Leitnaker et al<sup>6,7</sup> data, but it is not believed that significant differences would occur. The present agreement suggests that the heats of sublimation for zirconium and boron used in this report are essentially correct.

The Goldstein and Trulson<sup>31</sup> vaporization studies were performed with the aid of a mass spectrometer. They found a heat of formation of  $\text{ZrB}_2$  of  $\Delta H_{f298, \text{ZrB}_2}^\circ = -71.12 \text{ kcal/mole}$ , in good agreement with the calorimetric data already discussed. They also studied the equilibria



and derived

$$\Delta H_{f298, \text{ZrB}_2}^\circ = -72.73 \text{ kcal/mole}$$

At the present time, it is seen that vaporization studies give data in moderate agreement with calorimetric data. It should be pointed out that the vaporization studies require knowledge of the heats of sublimation of both zirconium and boron. Also, Gilles<sup>37</sup> has noted that there is still a discrepancy as far as the heat of sublimation of boron is concerned when one compares the Leitnaker *et al*<sup>6, 7</sup> data with the Goldstein and Trulson<sup>31</sup> data. The latter workers in common with most mass spectrometric people have found heats of sublimation for boron of  $\Delta H_{f298}^\circ \approx 130$  kcal/mole, whereas the workers using weight-loss methods prefer the somewhat higher values of 135 to 137 kcal/mole. At the present time, within the accuracy of the available data, it is felt that the heats of sublimation for Zr and B used in this report are probably adequate. It should be noted that the suggestion by Leitnaker *et al*<sup>6, 7</sup> that the heat of sublimation of zirconium should be markedly lowered appears to be incorrect.

The vaporization studies of Bolgar *et al*<sup>32</sup> were performed by Langmuir vaporization. Their data appear to be in serious error. For example, they discuss molecular species, whereas Goldstein and Trulson<sup>31</sup> clearly show that atomic species are the only important ones. The heat of sublimation found by Bolgar *et al*<sup>32</sup> is also invalid. They reported a value of 56.4 kcal/mole, whereas the expected value is about 475 kcal/mole. It should be pointed out that a rough Third Law calculation of one of their points gave about 440 kcal/mole for the heat of sublimation, but still the data compare poorly with the data already available.

The work of Buchler<sup>33</sup> was a preliminary study, and he concluded that calorimetric work was probably more accurate.

Earlier data on the heat of formation of  $ZrB_2$  by Brewer and Haraldsen<sup>38</sup> had indicated that  $\Delta H_{f298}^\circ ZrB_2 < -78$  kcal/mole via nitride equilibria. Brewer and Haraldsen found that  $ZrB_2$  is stable above 1820°K and is possibly stable to lower temperatures in nitrogen of about 0.5 atm.

Nowotny's<sup>39</sup> comment that  $ZrB_2$  becomes stable relative to TiN and BN formation above 1400°C (1673°K) is consistent with these data. These results can be compared to the analogous data for the  $TiB_2$ -nitrogen system by Williams<sup>40</sup> who found that a much higher temperature of 2150°K was required to make  $TiF_2$  stable relative to nitride formation. From these results, as shown by Brewer and Haraldsen,<sup>38</sup> it follows that the heat of formation of  $ZrB_2$  is more negative than that for  $TiB_2$ . These results are consistent with the data presently obtained.

Samsonov<sup>41, 42</sup> has reported a value of  $\Delta H_f^{\circ}{}_{298} = -63.1$  kcal/mole. In view of the recent, more precise, calorimetric data, these other determinations just discussed are not given further consideration.

### Supplement

Margrave<sup>43</sup> has indicated that the  $ZrB_2$  heat-content measurements<sup>19, 20</sup> will be published in the Journal of Chemical and Engineering Data. A melting point of 2790°C (3063°K) was observed by Engelke et al.<sup>44</sup> Kibler et al.<sup>45</sup> used vaporization studies of  $ZrB_2$  to derive  $\Delta H_f^{\circ}{}_{298.15} = -74.9$  kcal gfw<sup>-1</sup>.

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## 35.2 Zirconium Carbides

In this study, detailed analyses of zirconium carbides were made for  $\text{ZrC}_{(s, l)}$ . In addition to the references for this compound given below, other references may be found in sections VIII and IX (volume 2).

### 35.2.1 Zirconium Carbide ( $\text{ZrC}_{(s, l)}$ )

#### a. Crystal Structure and Melting Point

In the zirconium-carbon system, there is only one well established phase having the nominal composition  $\text{ZrC}$ . According to Hansen and Anderko,<sup>1</sup> this compound is cubic of the NaCl (B1) type structure. Lattice parameters listed by them vary from 4.678 to 4.695 Å, with the latter value preferred for the  $\text{ZrC}$  composition. Melting points of 3373° to 3473°K (3100° to 3200°C), 3803°K (3530°C), and 3448°K (3175°C) were listed in the same compilation. Additional data for this system, along with a phase diagram by Goldschmidt,<sup>2</sup> have been summarized by Schwarzkopf and Kieffer.<sup>3</sup>

More recent data for the lattice parameter of  $\text{ZrC}$  have been given by Sara and Dolloff<sup>4</sup> who found a value of 4.6821 Å which is somewhat smaller than the value of 4.69764 reported by Kempter and Fries.<sup>5</sup> According to data by Farr as discussed by Storms,<sup>6</sup> the lattice parameter for pure  $\text{ZrC}$  should be larger than 4.702 Å. Farr found this value for  $\text{ZrC}_{0.95}$ . Further data on the variation of  $\text{ZrC}$  lattice parameter as a function of composition and temperature have been reported by Dolloff and Sara.<sup>7</sup>

Recent phase diagrams for the  $\text{ZrC}$  system have been given by Benesovsky and Rudy<sup>8</sup> and Sara and Dolloff.<sup>4</sup> The region of  $\text{ZrC}$  melting has been further examined by Dolloff and Sara.<sup>7</sup> Their data show boundaries of the  $\text{ZrC}$  phase to exist near 38.5- and 49.9-atom-percent carbon at 3300°C. They also find that melting maximizes at 3420°C and approximately 46-atom-percent carbon. Incipient melting for the stoichiometric  $\text{ZrC}$  would be somewhat lower at about 3375°C, and the liquidus for this composition would be at ~3410°C. These data were read from their figure 5.

For the purposes of the table preparation, the assumption will be made that stoichiometric  $\text{ZrC}$  melts at a single temperature, and the value of 3420°C (3693°K) listed by Dolloff and Sara<sup>7</sup> for the composition at 46-atom-percent carbon will be used. This choice of melting temperature for  $\text{ZrC}$  is compatible with an observation by Nowotny<sup>9</sup> that the higher reported melting points are preferred to the lower ones, such as 3100° to 3200°C and 3175°C reported earlier. Nowotny<sup>9</sup> made his observation on the basis of an empirical rule that the product of expansion coefficient times melting point is a constant. Further discussions of this rule and melting phenomena are given in works by Neshpor and Samsonov<sup>10</sup> and Nowotny.<sup>11</sup>

## b. Thermodynamic Properties

### 1) Heat of fusion

The very high melting point of ZrC makes it very difficult to measure the heat of fusion of this compound. Accordingly, it is necessary to estimate this quantity. A procedure based on Kubaschewski and Evans<sup>12</sup> (p. 192) suggests that the entropy change for fusion of NaCl-type lattices is  $3 \text{ cal deg K}^{-1} \text{ g atom}^{-1}$  or  $6 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  for the molecule. Using these data together with the accepted melting point of  $3693^\circ\text{K}$  gives a heat of fusion of ZrC of  $22158 \text{ cal/mole}$ . However, Kubaschewski and Evans show that covalent bonding as contrasted to ionic bonding leads to somewhat lower entropies of fusion. In view of the large uncertainty existing and the fact that ZrC shows more covalent bonding, a somewhat lower value was chosen. This was "rounded off" to give  $20,000 \pm 5000 \text{ cal/mole}$  as the heat of fusion. The "effective" entropy of fusion implied by this choice is thus  $5.415 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  or  $2.707 \text{ cal deg K}^{-1} \text{ g atom}^{-1}$ .

### 2) Entropy and heat content at $298.15^\circ\text{K}$

Westrum<sup>13</sup> has measured the low-temperature heat capacity of a specimen of zone-refined ZrC. His data yield  $S_{298.15}^\circ = 7.964 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ ,  $H_{298}^\circ - H_0^\circ = 1401 \text{ cal/mole}$  and  $C_{p,298.15}^\circ = 9.058 \text{ cal/mole}^\circ\text{K}$ . These data were used here and supersede earlier estimated values of  $S_{298.15}^\circ = 9.3 \pm 0.3 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  by Kelley and King,<sup>14</sup>  $7.9 \pm 0.5 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  by Krikorian,<sup>15</sup>  $9.0 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  by Kaufman and Bernstein,<sup>16</sup> and  $8.1 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  estimated herein. This present work uses a technique similar to that utilized by Krestovnikov and Vendrikh<sup>17</sup> for  $\text{TiB}_2$ . Melting-point data for the component elements and the compound are used along with density data for the elements to calculate effective Debye temperatures of the component elements in the compound by means of the Lindemann equation. Other data derived for ZrC with these empirical calculations gave  $C_{p,298}^\circ = 8.079 \text{ cal/mole}^\circ\text{K}$  and  $H_{298}^\circ - H_0^\circ = 1340 \text{ cal/mole}$  in fair agreement with the experimental data.

### 3) High-temperature heat content

There is a limited amount of experimental high-temperature heat-capacity data for ZrC. Margrave<sup>18</sup> reports drop-calorimetry enthalpy data for the range  $300^\circ$  to  $1200^\circ\text{K}$  and gives an equation for heat capacity of the form

$$C_p^\circ = 11.40 + 1.42 \times 10^{-3}T - 18.67 \times 10^{-4}T^{-2} \text{ cal/mole}^\circ\text{K} \quad (\text{IVB35, 2, 1-1})$$



Drop calorimetry has also been performed at the Southern Research Institute<sup>19</sup> for the temperature range 500° to 4700°F. Their equation converted to cgs units is

$$C_p^\circ = 17.498 - 8.583 \times 10^{-3}T + 3.221 \times 10^{-6}T^2 \text{ cal/mole } ^\circ\text{K} \quad (\text{IVB35. 2. 1-2})$$

Pulse-heating techniques were used at Avco<sup>20</sup> for the range 1639° to 2499°K. The  $C_p^\circ$  data were considerably higher than the Southern Research Institute data over the same temperature range.

Kelley<sup>21</sup> has not listed any high-temperature heat-capacity data for ZrC. Krikorian<sup>15</sup> has derived a heat-capacity equation by comparison with other carbides, and by use of values of  $S_{298}^\circ$  for the respective carbide.

For the present purposes, the data of Krikorian were modified by using the experimental heat-capacity value of Westrum<sup>13</sup> at 298.15; i. e.,  $C_{p,298.15}^\circ = 9.058 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$  in conjunction with Westrum's  $S_{298.15}^\circ$  value of  $7.964 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$  to calculate  $C_{p,1000^\circ\text{K}}^\circ = 13.282 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$ , and  $C_{p,2000^\circ\text{K}}^\circ = 15.685 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1}$ . These data at these three temperatures were then utilized to give an equation

$$C_p^\circ = 11.336 + 2.207 \times 10^{-3}T - 2.610 \times 10^{-5}T^2 \text{ cal mole}^{-1} \text{ } ^\circ\text{K}^{-1} \quad (\text{IVB35. 2. 1-3})$$

In table 73, the data obtainable from the various sources already described have been summarized. It is seen that the present calculations, using the Westrum-Krikorian data, give a reasonable interpretation of the high-temperature behavior of ZrC. That is, the actually measured enthalpy-content data of the Southern Research Institute and the calculated Margrave<sup>18</sup> data agree fairly well with the present results. Furthermore, the free-energy function data of Margrave and the present calculations are in good agreement. The present calculations give  $C_p^\circ$  values which increase uniformly with temperature, whereas the original Southern Research Institute equation (although it reproduces enthalpy contents) shows a dip in  $C_p^\circ$  as temperature is raised.

Thus, the adopted equation is considered to give a reasonable representation of the experimental data currently available.

#### 4) Standard heat of formation

A heat-of-combustion measurement for ZrC has been made by Mah and Boyle.<sup>22</sup> The specimen of ZrC used contained 11.07-percent carbon and 88.15-percent zirconium contrasted with a theoretical 11.63-percent carbon and 88.37-percent zirconium. In correcting their results, Mah and Boyle had assumed ZrC

TABLE 73

## COMPARISON OF VARIOUS DATA FOR ZrC

Temperature	Source	$C_p^\circ$	$S_T^\circ$	$-\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$
$^\circ\text{K}$		$\text{cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$	$\text{cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$	$\text{cal}^\circ\text{K}^{-1}\text{gfw}^{-1}$	$\text{kcal gfw}^{-1}$
298.15	1. Present Calculations	9.058	7.964	7.964	0.0
	2. Margrave Equation	9.723	7.964	7.964	0.0
	3. So. Res. Inst. (Experimental)	---	---	---	0.0
	4. So. Res. Inst. (Equation)	15.225	7.964	7.964	0.0
1000	1. Present Calculations	13.282	21.894	13.547	8.347
	2. Margrave Equation	12.633	21.800	13.591	8.208
	3. So. Res. Inst. (Experimental)	---	---	---	$\sim 8.0^*$
	4. So. Res. Inst. (Equation)	12.136	24.583	15.167	9.416
2000	1. Present Calculations	15.685	31.860	20.429	22.863
	2. Margrave Equation	14.193	31.052	20.229	21.645
	3. So. Res. Inst. (Experimental)	---	---	---	$\sim 21.0^*$
	4. So. Res. Inst. (Equation)	13.216	32.960	22.182	21.555
	5. Innat-Avco	20.6	---	---	---

\* Estimated from their tabulated, experimental enthalpy contents.

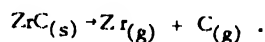
## Notes:

1. Present Calculations -- Using equation derived from Westrum's low-temperature data<sup>13</sup> and Krikorian's estimates.<sup>15</sup>
2. Margrave Equation --  $C_p^\circ = 11.40 + 1.42 \times 10^{-3}T - 18.67 \times 10^{-4}T^{-2} \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .
3. So. Res. Inst. (Experimental) -- Data from Neel et al.<sup>19</sup>
4. So. Res. Inst. (Equation) --  $C_p^\circ = 17.498 - 8.583 \times 10^{-3}T + 3.221 \times 10^{-6}T^2 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .
5. Innat-Avco -- Experimental pulse-heating value from Barriault et al.<sup>20</sup>

was ~94 percent of the specimen with the remainder present as ZrN and free carbon or zirconium oxide and free carbon. From their data, they obtained a value of  $\Delta H_{298.15, \text{ZrC}}^\circ = -44.1 \pm 1.5$  kcal/mole. From the fact that their specimen had such a large amount of impurities, it would seem that the data may need further verification.

Vaporization experiments on ZrC have been reported by Pollock,<sup>23</sup> Coffman, Kibler, Lyon, and Acchione,<sup>24</sup> Fujishiro and Gokcen,<sup>26</sup> and by Bolgar, Verkhoglyadova, and Samsonov.<sup>27</sup> Pollock's experiment covered the range 2620° to 2747°K by means of Knudsen and Langmuir techniques. At 2675°K, he found the standard free energy of formation to be  $-38.9 \pm 1.5$  kcal/gfw and had good agreement between Knudsen-cell experiments and Langmuir vaporization.

Pollock's Langmuir data (six temperatures) were recalculated by a Third-Law technique according to the reaction:



The results of these calculations are summarized below.

TABLE 74

THIRD-LAW ANALYSIS OF POLLOCK'S LANGMUIR DATA FOR ZrC

T	P <sub>Zr</sub>	P <sub>C</sub>	$\Delta F_T^\circ$	T ( $\Delta fef$ )	$\Delta H_{298}^\circ$
°K	10 <sup>7</sup> atm	10 <sup>8</sup> atm	cal gfw <sup>-1</sup>	cal gfw <sup>-1</sup>	cal gfw <sup>-1</sup>
2673	2.23	6.0	169,689	192,645	362,334
2671	1.94	6.0	170,303	192,501	362,804
2674	2.39	7.3	168,345	192,718	361,063
2747	5.4	16.3	164,104	197,805	361,909
2641	1.56	4.8	170,704	190,410	361,114
2647	1.51	4.7	171,375	190,830	362,205
Average 361,904					

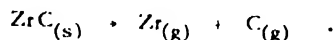
In the above calculation,  $\Delta fef = fef_{\text{Zr}(g)} + fef_{\text{C}} - fef_{\text{ZrC}(s)}$ , where  $fef_{\text{Zr}} = (F_T^\circ - H_{298}^\circ)/T$ . Values for  $fef_{\text{Zr}(g)}$  and  $fef_{\text{ZrC}(s)}$  were taken from recent calculations of the present report, while values for  $fef_{\text{C}(g)}$  were from an earlier report.<sup>28</sup>

Thus, the Langmuir data of Pollock indicate that the heat of sublimation of ZrC is  $\Delta H_{298}^{\circ} = 361.904$  kcal/gfw. Using, as heat-of-sublimation data at 298.15°K, values from the same sources as the free-energy functions for the elements, the heat of formation of ZrC at 298.15°K is calculated next, as follows:

$$\begin{aligned}\Delta H_{f, \text{ZrC}, 298.15}^{\circ} &= -\Delta H_{\text{sub}, \text{ZrC}}^{\circ} + \Delta H_{\text{sub}, \text{Zr}}^{\circ} + \Delta H_{\text{sub}, \text{C}}^{\circ} \\ &= -361.904 + 143.126 + 170.890 \\ &= -47.888 \text{ kcal/mole} \quad (\text{IVB35. 2. 1-4})\end{aligned}$$

This result is essentially equivalent to the value of -47.7 kcal/mole obtained by Pollock. The agreement is somewhat fortuitous since the present calculations use newer free-energy functions for ZrC and also a lower heat of sublimation for Zr. No further analysis was performed on Pollock's Knudsen-cell data since he showed, by use of his own internally consistent data, that the Knudsen-cell and Langmuir data were equivalent.

The vaporization data of Coffman et al<sup>25</sup> were obtained by a Langmuir technique. Their partial pressure data for  $\text{Zr}_{(g)}$  and  $\text{C}_{(g)}$ ; yielded a value of  $\Delta F_{2740}^{\circ} \text{K} = 164.7$  kcal/mole for the reaction:



Using free-energy functions for  $\text{ZrC}_{(s)}$ ,  $\text{Zr}_{(g)}$ ,  $\text{C}_{(g)}$  from the same sources as before, one has:

TABLE 75

FREE-ENERGY FUNCTIONS FOR  $\text{ZrC}_{(s)}$ ,  $\text{Zr}_{(g)}$ , AND  $\text{C}_{(g)}$  AT 2600°, 2700°, AND 2800°K

T	fef $\text{ZrC}_{(s)}$	fef $\text{Zr}_{(g)}$	fef $\text{C}_{(g)}$	$\Delta$ (fef)
°K	cal deg K <sup>-1</sup> gfw <sup>-1</sup>		cal deg K <sup>-1</sup> gfw <sup>-1</sup>	
2600	23.576	51.578	44.131	72.133
2700	24.054	51.803	44.298	72.047
2800	24.520	52.021	44.461	71.962

From these data, one obtains  $\Delta$ (fef) = 72.013 cal deg K<sup>-1</sup> gfw<sup>-1</sup>. Thus,

$$\begin{aligned}\Delta H_{298.15}^{\circ} &= \Delta F_T^{\circ} + T \Delta$$

$$\begin{aligned}&= 164,700 + 2740 \times 72.013 \text{ cal/mole} \\ &= 362.015 \text{ kcal/mole} \quad (\text{IVB35. 2. 1-5})\end{aligned}$$

for the heat of sublimation of ZrC. The agreement between this value and that of Pollock is extremely good. Using the other data already cited for standard heats of sublimation of Zr and C, one obtains finally a standard heat of formation of ZrC as:

$$\Delta H_{f298.15, \text{ZrC}}^{\circ} = -362.015 + 143.126 + 170.890$$

$$= -47.999 \text{ kcal/mole.} \quad (\text{IVB35. 2. 1-6})$$

Thus on the basis of these different determinations, Pollock's Knudsen experiment and the two independent Langmuir experiments of Pollock and Coffman et al, it may be concluded that the standard heat of formation of ZrC is -48.0 kcal/mole. Data which can contribute to uncertainties in this value are the errors in the experimental vapor pressures, in the free-energy functions for  $\text{Zr}_{(s)}$ ,  $\text{Zr}_{(g)}$ ,  $\text{C}_{(g)}$ , and the heats of sublimation for Zr and C.

If Pollock's conclusion that Knudsen-cell data give data in agreement with Langmuir data is accepted, it would seem that corrections for condensation coefficient are unnecessary. The agreement between the data of Pollock and Coffman et al suggests that the vapor-pressure data are reasonably correct. Furthermore, the free-energy functions for  $\text{Zr}_{(g)}$  and  $\text{C}_{(g)}$  should be fairly reliable. The remaining quantities which contribute uncertainties are listed below.

Quantity	Uncertainty
	kcal/gfw
Zr (sub)	$\pm 3$
C (sub)	$\pm 0.5$
$T \times \Delta(f) \text{ ZrC}$	$\pm 2$
Total Uncertainty	$\pm 5.5$

Thus, the standard heat of formation of ZrC from this analysis is accepted as  $\Delta H_{f298.15, \text{ZrC}}^{\circ} = -48.0 \pm 5 \text{ kcal/mole}$ . It should be noted that, if the heat of formation value for  $\text{Zr}_{(g)}$  is reduced from 143.126 kcal gfw<sup>-1</sup> to a lower value, the heat-of-formation value for ZrC becomes more negative. It has been suggested by Leitnaker et al<sup>29</sup> that the heat of sublimation of Zr should be lowered. The value of 143.126 used here is an average of two determinations, one of which was not available when Leitnaker et al published their paper. Accordingly,

it is improbable that the heat of sublimation of Zr could be lowered very much, but the uncertainty of this value is clearly at least  $\pm 3$  kcal/gfw at the present time. Further details of the problem of Zr vaporization are discussed in the section devoted to zirconium.

Additional vaporization studies include the resonance-line absorption work by Coffman et al.<sup>25</sup> They found that the zirconium vapor pressure over ZrC at 2740°K was equal to that over pure Zr at 2144°K. From the data for pure Zr accepted in the present compilation, it is found that

$$\Delta F_{Zr, 2144}^{\circ} = 72.673 \text{ kcal/mole} \quad (\text{IVB35. 2. 1-7})$$

and

$$P_{Zr} = 10^{-7.407} \text{ atm.} \quad (\text{IVB35. 2. 1-8})$$

Thus, for the reaction,



at 2740°K,

$$\begin{aligned} \Delta F^{\circ} &= -4.575 \times 2740 \times (-7.407) \\ &= +92867 \text{ cal/gfw.} \end{aligned} \quad (\text{IVB35. 2. 1-10})$$

Then using the following free-energy functions:

TABLE 76  
FREE-ENERGY FUNCTIONS FOR  $ZrC_{(s)}$ ,  $Zr_{(g)}$ , AND  
 $C_{(s)}$  AT 2700° AND 2800°K

T	$f_{ef}ZrC_{(s)}$	$f_{ef}Zr_{(g)}$	$f_{ef}C_{(s)}$	$\Delta(f_{ef})$
°K	cal degK <sup>-1</sup> gfw <sup>-1</sup>		cal degK <sup>-1</sup> gfw <sup>-1</sup>	
2700	24.054	51.803	6.826	34.575
2800	24.520	52.021	6.997	34.498

one finds that

$$\Delta(f_{ef}) = 34.545 \text{ at } 2740^{\circ}\text{K} \quad , \quad (\text{IVB35. 2. 1-11})$$

and

$$T \Delta(f_{ef}) = 2740 \times 34.545 = 94653 \text{ cal/gfw.} \quad (\text{IVB35. 2. 1-12})$$

Finally,

$$\begin{aligned}\Delta H_{298}^{\circ} &= \Delta F^{\circ} + T \Delta f_{ef} \\ &= 92,867 + 94,653 \text{ cal/gfw,} \quad (\text{IVB35. 2. 1-13})\end{aligned}$$

or

$$\Delta H_{298}^{\circ} = 187,520 \text{ cal/mole.} \quad (\text{IVB35. 2. 1-14})$$

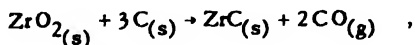
Since

$$\Delta H_{298}^{\circ} = 187,520 = \Delta H_{\text{sub,Zr}}^{\circ} - (\Delta H_{\text{f,ZrC}}^{\circ}), \quad (\text{IVB35. 2. 1-15})$$

$$\begin{aligned}\Delta H_{\text{f,298.15,ZrC}}^{\circ} &= -187,520 + 143,126 \\ &= -44,394 \text{ kcal/mole.} \quad (\text{IVB35. 2. 1-16})\end{aligned}$$

The vaporization experiments of Bolgar et al<sup>27</sup> gave results in serious disagreement with work already reported. They gave a heat of sublimation for ZrC of only 52.2 kcal/gfw as contrasted with values already calculated of about 362 kcal/gfw. Their data were obtained by a Langmuir method, and apparently they used a Second-Law method to evaluate their data. One of their tabulated pressures has been used with a Third-Law treatment, and although more realistic values were obtained, the data still made ZrC far too unstable. Hence, their work was not considered further. Similarly, Pollock has shown that the work of Fujishiro and Gokcen<sup>26</sup> gives serious errors, and hence it was not considered further here.

A third type of data which has been used to derive heat-of-formation values for ZrC is equilibrium data in the Zr-C-O system. Prescott,<sup>30</sup> Kutsev et al,<sup>31, 32</sup> Zhelankin et al,<sup>33</sup> and Lorenz and Woolcock<sup>34</sup> have studied this system. Prescott<sup>30</sup> studied the ZrO<sub>2</sub>-C system in the range 1800° to 2015°K for CO pressures of 0.522 to 2.32 atm. Lorenz and Woolcock<sup>34</sup> obtained their data at 1743°K. Kutsev et al<sup>31</sup> have criticized these earlier works, saying that the equilibrium phases were improperly confirmed. The Russian workers claim that ZrC exists as an oxycarbide of the composition ZrC<sub>0.71</sub>O<sub>0.08</sub>. Their measurements were performed in the temperature range 1814° to 2020°K with pressures of CO varying from 115 to 935 mm Hg. They calculated that  $\Delta H_{\text{f,298.15,ZrC}_{0.71}\text{O}_{0.08}}^{\circ} = -53.8 \text{ kcal/gfw}$ . A re-calculation of one of their data points at 1900°K, assuming the equilibrium



was made. Thermodynamic data for CO were from the JANAF tables,<sup>35</sup> for C and ZrC from the present work,<sup>28</sup> and for ZrO<sub>2</sub> from Kelley et al.<sup>14, 36</sup> The heat-of-formation value for ZrO<sub>2</sub> of -261.5 kcal/mole was based on the work of Humphrey.<sup>37</sup> Assumptions were made that the activity of ZrO<sub>2</sub> = activity of ZrC = 1. These data yielded  $\Delta H_{f298.15}^\circ = -41.284$  kcal/mole for the heat of formation of ZrC. No additional points were re-calculated. A similar calculation by Pollock<sup>23</sup> for Prescott's<sup>30</sup> data yielded  $\Delta H_{f298.15}^\circ = -46.5$  kcal/gfw. The difference in the  $\Delta H_{f298}^\circ$  values from Prescott and Kutsev et al.<sup>31</sup> is consistent, in that Prescott observed pressures twice as large as those of Kutsev et al.

In view of the uncertainties raised by Kutsev et al. as to the actual phases and hence the activities of the species, it is felt that accurate data cannot yet be obtained from these measurements. Thus, Meerson and Samsonov<sup>38</sup> have claimed that intermediate phases of Zr<sub>2</sub>O<sub>3</sub> and ZrO exist in the Zr-C-O system. Further illustration of the problems in this system is shown by the work of Zhelankin et al.,<sup>33</sup> where the system becomes bivariant at higher temperatures (2203° to 2803°K). For this situation, the two separate phases ZrO<sub>2</sub> and ZrC become a single-phase ZrC<sub>x</sub>O<sub>y</sub>. It is even more difficult to evaluate the activities of the carbides and oxides under such circumstances.

In summarizing the available data for the heat of formation of ZrC, it is difficult to give an accurate value. Listed below are the values obtained.

TABLE 77  
SUMMARY OF HEATS OF FORMATION OF ZrC  
EVALUATED AT RAD

Type of Experiment	Reference	$\Delta H_{f298.15}^\circ$
Vaporization-Langmuir	Pollock <sup>23, 24</sup>	kcal/gfw -47.8
Vaporization-Knudsen	Pollock <sup>23, 24</sup>	~ -48.0
Vaporization-Langmuir	Coffman <u>et al.</u> <sup>25</sup>	-48.0
Vaporization-Atomic Absorption	Coffman <u>et al.</u> <sup>25</sup>	-44.4
Combustion	Mah and Boyle <sup>22</sup>	-44.1
ZrO <sub>2</sub> -C-ZrC-CO Equilibrium	Prescott <sup>30</sup>	-46.0
ZrO <sub>2</sub> -C-ZrC-CO Equilibrium	Kutsev <u>et al.</u> <sup>31</sup>	~ -41.0



Ordinarily the heat-of-combustion measurement should be given considerable weight. However, because of the impurity in the ZrC specimen used for combustion and because of the agreement between three independent vaporization studies, the more negative value of  $-48.0 \pm 5.0$  kcal/mole is accepted as  $\Delta H_{f298.15}^\circ$ . This value is about 4 kcal/mole more negative than the heat-of-combustion value but is consistent with a value of -50 kcal/mole predicted by Ormont<sup>39</sup> in 1959. It is clear from this review and analysis that more precise work is needed for the ZrC heat of formation.

### Supplement

Preliminary vaporization studies of ZrC have been made by Blackburn.<sup>40</sup> A sample of zirconium-rich carbide was sent to Kelley for a heat-of-combustion determination.<sup>41</sup> Engelke et al<sup>42</sup> observed melting at 3560°C (3833°K).

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### 35.3 Zirconium Nitrides

#### Phase Diagram and General Information

Hansen and Anderko<sup>1</sup> show a phase diagram for the Zr-N system based on the work of Domagala et al.<sup>2</sup> The only compound formed appears to be the ZrN phase which has a fairly wide range of homogeneity. Reported compounds such as  $\text{Zr}_3\text{N}_2$ ,  $\text{Zr}_3\text{N}_4$ ,  $\text{Zr}_2\text{N}_3$ , and  $\text{Zr}_3\text{N}_8$  do not exist. Relatively recently, Storms<sup>3</sup> has reviewed the phase data for the Zr-N system and also concludes that cubic ZrN is the only compound formed in this system.

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#### 35.3.1 Zirconium Nitride ( $\text{ZrN}_{(s, \ell)}$ )

##### a. Crystal Structure and Melting Point

Hansen and Anderko<sup>1</sup> have noted that ZrN has a cubic structure isotypic with NaCl. The lattice parameter  $a = 4.575\text{\AA}$  appears to be typical. Schonberg<sup>2</sup> found lower lattice parameters in the range 4.537 to 4.562  $\text{\AA}$  and suggested that higher values were due to the presence of oxygen in the lattice. Storms<sup>3</sup> notes that above  $\text{ZrN}_{0.78}$  the lattice parameter remains constant at 4.577  $\text{\AA}$ , but that removal of nitrogen (i. e.,  $\text{ZrN}_{0.78-x}$  formation) causes an expansion of the lattice leading to  $a = 4.584\text{\AA}$  at the lower phase boundary. Storms suggests that the wide range of reported lattice parameters may be due to some factor other than dissolved oxygen.

Smagina, Kutsev, and Ormont<sup>4</sup> found the homogeneity range of the ZrN phase to extend from  $\text{ZrN}_{0.56}$  to  $\text{ZrN}_{1.0}$ . Rudy and Benesovsky<sup>5</sup> found the lower phase limit to be  $\text{ZrN}_{0.55}$  at 1500°C.

Additional recent work on the ZrN phase, which concerns lattice-parameter measurements, includes the works of Kibler et al.,<sup>6</sup> Smagina and Kutsev,<sup>7</sup> and Smagina et al.<sup>8</sup>

Melting points of 2930°C (3203°K) by Friederich and Sittig<sup>9</sup> and 2980°C (3253°K) by Agte and Moers<sup>10</sup> have been reported. The latter value is accepted in this work.

## b. Thermodynamic Properties

### 1) Heat capacity and entropy at 298.15°K

Todd<sup>11</sup> has measured the heat capacity of ZrN for the range 53° to 297°K. Kelley and King<sup>12</sup> have used Todd's data and tabulate  $S_{298.15}^{\circ} = 9.29 \pm 0.05$  e. u. An integration of the Todd data was performed in the present work so as to evaluate  $H_{298.15}^{\circ} - H_0^{\circ} = 1.575$  kcal gfw<sup>-1</sup>. In this work, the value  $S_{298.15}^{\circ} = 9.29$  e. u. has been accepted. However, it is possible that because of lattice defects there may be a zero-point entropy. Thus, Smagina and Kutsev<sup>7</sup> have noted that disorder exists in the ZrN phase. However for the present work, no attempt has been made to correct the entropy data, realizing that future work may make revision necessary.

### 2) High-temperature heat content

Kelley<sup>13</sup> tabulates a heat-capacity relation for ZrN based on the work of Coughlin and King.<sup>14</sup> The equation is

$$C_p^{\circ} = 11.10 + 1.68 \times 10^{-3}T - 1.72 \times 10^{-5}T^2 \text{ cal degK}^{-1}\text{gfw}^{-1},$$

for the range  $298^{\circ}\text{K} \leq T \leq 1700^{\circ}\text{K}$ .

Hedge et al<sup>15</sup> reported enthalpy measurements in the range 481° to 4530°F (540° to 2790°K) and gave an expression of the form

$$H_t - H_{80^{\circ}\text{F}}^{\circ} = -5.9 + 89.2 \times 10^{-3}t + 11.7 \times 10^{-6}t^2 - 0.91 \times 10^{-9}t^3 \text{ Btu/lb},$$

where  $t = ^{\circ}\text{F}$ .

At their highest temperature, 4530°F (2790°K), Hedge et al<sup>15</sup> found  $H_t - H_{80^{\circ}\text{F}}^{\circ} = 546$  Btu/lb, or  $H_t^{\circ} - H_{298.15^{\circ}\text{K}}^{\circ} = 31,919$  cal gfw<sup>-1</sup>. This may be compared with a value of  $H_{2800}^{\circ} - H_{298.15}^{\circ} = 33,766$  cal gfw<sup>-1</sup> calculated from the extrapolated Kelley<sup>13</sup> equation. Thus, the Hedge et al enthalpy data are about 5.8 percent lower than the Kelley data at 2790°K.

Neel et al<sup>16</sup> have measured enthalpy-content data for the range

533° to 2927°K. Their data after converting to cgs units are shown below. In converting their data, a small correction of  $H_{298.15}^{\circ} - H_0^{\circ} = 237 \text{ cal gfw}^{-1}$  was used based on integration of the low-temperature data of Coughlin and King.<sup>14</sup>

A treatment of the Neel et al data by the Shomate method with  $C_p, 298.15 = 9.655 \text{ cal degK}^{-1} \text{ gfw}^{-1}$  leads to the equation

$$C_p^{\circ} = 8.0314 + 0.36989 \times 10^{-2}T + 0.46291 \times 10^{-5}T^{-2} \text{ cal degK}^{-1} \text{ gfw}^{-1}.$$

#### ENTHALPY DATA FROM NEEL et al<sup>16</sup>

T	$H_T^{\circ} - H_{298.15}^{\circ}$
°K	cal gfw <sup>-1</sup>
533.7	2574.9
533.7	2142.3
813.7	4410.5
819.8	4936.7
1086.4	9525.8
1088.1	8999.6
1321.4	12156.5
1372.5	12741.1
1618.1	14202.5
1944.2	19463.0
2283.1	28700.6
2322.0	25719.1
2560.9	31331.3
2688.7	30220.6
2927.5	35657.3

Referring to the enthalpy data from Neel et al,<sup>16</sup> it may be seen that at 2927°K the value 35,657 cal gfw<sup>-1</sup> compares favorably with a value of 35,353 cal gfw<sup>-1</sup> calculated from the Kelley equation at 2900°K. It may also be noted that the Neel et al data show a rather large deviation; i.e., their experimental enthalpies showed wide fluctuations from the smoothed enthalpies computed using  $C_p^{\circ}$  relation directly above.

For the present work, it appears that the Kelley<sup>13</sup> data can be safely extrapolated to high temperatures and give reasonable agreement with the more recent measurements. Accordingly, the Kelley equation is used in the present work and is extrapolated to the melting point at 3253°K. The heat of fusion is estimated to be 20.0 kcal gfw<sup>-1</sup> and the heat capacity of liquid ZrN is assumed to be 16.0 cal degK<sup>-1</sup> gfw<sup>-1</sup>.

### 3) Heat of formation

The heat-of-formation of ZrN has been determined by Mah and Gellert<sup>17</sup> by combustion calorimetry to give  $\Delta H_{f298.15}^{\circ} = -87.3 \pm 0.4$  kcal gfw<sup>-1</sup>. The heat-of-formation value accepted in this work for ZrO<sub>2</sub>, i. e.,  $\Delta H_{f298.15}^{\circ} = -261.5$  kcal gfw<sup>-1</sup>, was utilized by Mah and Gellert. Using this same value for ZrO<sub>2</sub>, the earlier heats of combustion of Neumann et al<sup>18</sup> yield -85.5 kcal gfw<sup>-1</sup> and of Smagina et al<sup>4</sup> yield -87.9 kcal gfw<sup>-1</sup>. The latter workers also obtained values of heat of formation in the range of compositions ZrN<sub>0.56</sub> to ZrN<sub>1.0</sub>. Their heats varied from -56.1 to -87.9 kcal gfw<sup>-1</sup> in this range. It is seen that the calorimetry data give good agreement for the stoichiometric composition of interest here. For the present work, the value found by Mah and Gellert<sup>17</sup> is accepted. Vaporization experiments as described in the next section have not yielded accurate data to evaluate the heat of formation.

### 4) Vaporization data

Vaporization experiments have been performed by Hoch et al,<sup>19</sup> Smagina et al,<sup>8</sup> and Kibler et al.<sup>6</sup> Hoch et al<sup>19</sup> used Knudsen effusion in the range 2236° to 2466°K and obtained  $\Delta H_{f298.15}^{\circ}$ , ZrN = -80.43 kcal gfw<sup>-1</sup>. They had assumed that vaporization of ZrN produces solid Zr and gaseous N<sub>2</sub>. However, Smagina et al<sup>8</sup> note that this reaction was not confirmed. Because of the wide homogeneity range of the ZrN<sub>x</sub> phase, it is not likely that the reaction is univariant as assumed by Hoch et al.<sup>19</sup> Rather, the works of Smagina et al<sup>8</sup> and Kibler et al<sup>6</sup> show that the N<sub>2</sub> pressure varies greatly with composition of the ZrN<sub>x</sub> phase. However, considerable disagreement exists between the latter two works also. Thus, Kibler et al<sup>6</sup> performed effusion measurements, and Smagina et al<sup>8</sup> used tensimetric measurements in the higher-pressure range of 0.1 to 100 mm Hg. The pressure data obtained by Smagina et al for a range of compositions ZrN<sub>0.7</sub> to ZrN<sub>0.96</sub> are considerably higher than the comparable Kibler et al data.

Fesenko and Bolgar<sup>20</sup> performed Langmuir vaporization experiments in the range 2236° to 2466°K, but did not consider the effect of composition changes. Akishin and Khodiev<sup>21</sup> have made mass-spectrometric studies of the vaporization of ZrN.

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### 35.4 Zirconium Oxides

In this study, detailed analyses of zirconium oxides were made for  $\text{ZrO}(\text{g})$ ,  $\text{ZrO}_2(\text{s}, \text{l})$  and  $\text{ZrO}_2(\text{g})$ . In addition to the references for these compounds given below, other references may be found in sections VIII and IX (volume 2).

#### 35.4.1 Zirconium Monoxide ( $\text{ZrO}(\text{g})$ )

##### a. Thermodynamic Functions

The spectroscopic data available for  $\text{ZrO}(\text{g})$  indicate that the energy levels for this molecule are still incompletely known. More recent work has indicated several changes in the 1950 tabulation by Herzberg.<sup>1</sup> Some of the lower levels found by Herzberg are shown in table 78. Additional data have been given by Rosen,<sup>2</sup> and the lower levels he tabulated are listed in table 79.

TABLE 78

SPECTROSCOPIC CONSTANTS FOR ZIRCONIUM MONOXIDE (gas)  
FROM HERZBERG<sup>1</sup> (1950)

State	$T_e$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e x_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$a_e$ ( $\text{cm}^{-1}$ )	$r_e$ ( $10^{-8}\text{cm}$ )
$\Lambda^3\Sigma$	16088.9	853.9	3.14	0.565	0.0077	1.481
$a^1\Sigma$	$a = ?$	978.0	5.04	---	----	---
$X^3\pi$	605.1 297.2 0	936.6	3.45	0.618	0.0070	1.416

TABLE 79

SPECTROSCOPIC CONSTANTS FOR ZIRCONIUM MONOXIDE (gas)  
FROM ROSEN<sup>2</sup> (1951)

State	$T_e$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$\omega_e x_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$a_e$ ( $\text{cm}^{-1}$ )	$r_e$ ( $10^{-8}\text{cm}$ )
$\Lambda^3\Sigma$	16088.9	853.9	3.14	0.5658	0.0077	1.4812
$c^1\Sigma$	9170	938.1	1.80	----	----	----
$a^1\Sigma$	1300	978.07	5.04	----	----	----
$X^3\pi$	605.1 297.2 0	936.5	3.47	0.6244 0.6186 0.6149	0.106 0.045 0.06	1.4099 1.4165 1.4208

Some of the more important band systems studied for the ZrO molecule are shown in table 80. These data have been taken from the compilation by Rosen.<sup>2</sup>

TABLE 80

SOME BANDS STUDIED FOR ZIRCONIUM MONOXIDE  
FROM ROSEN<sup>2</sup> (1951)

Name of System	Type of Transition*	Wavelength Region (Å)
$\phi$	$E (^3\pi) \rightarrow (X)^3 \pi$	3120 to 2940
$\delta$	$D \rightarrow (X)^3 \pi$	3508 to 3472
A **	$b (^1\Sigma) \rightleftharpoons a (^1\Sigma)$	4000 to 3390
a	$C (^3\pi) \rightleftharpoons (X)^3 \pi$	5600 to 4200
B ***	$b (^1\Sigma) \rightarrow c (^1\Sigma)$	5450 to 4970
$\beta$	$B \rightleftharpoons (X)^3 \pi$	5810 to 5455
$\gamma$	$A (^3\Sigma) \rightleftharpoons (X)^3 \pi$	7600 to 5110

\* Based primarily on work of Afaf<sup>3</sup> (1950).

\*\* Uhler and Akerlind<sup>4</sup> (1956) discuss the possibility of the singlet system A being a  $^1\Delta$ - $^1\Delta$  transition although they say it is probably  $^1\Sigma$ - $^1\Sigma$ .

\*\*\* Akerlind<sup>5</sup> (1956) considers system B to be either a  $^1\Sigma$ - $^1\Sigma$  or a  $^1\Delta$ - $^1\Delta$  transition. He considers the upper state to be  $d^1\Sigma$  rather than  $b^1\Sigma$  as Afaf<sup>3a</sup> has concluded because this state differs from the upper state of system A.

In table 79, the data for the singlet state  $a^1\Sigma$  listed by Rosen<sup>2</sup> come from the work of Afaf<sup>3</sup>, who has studied the arc spectrum of ZrO in the ultraviolet, the visible, and the infrared. Afaf has considered the ground state of ZrO to be  $^3\pi$  and estimates the  $a^1\Sigma$  state to be a low-excited state 1300 cm<sup>-1</sup> higher. The  $c^1\Sigma$  state listed by Rosen is estimated by Rosen and is considered by him to be uncertain.

In the compilations of Herzberg<sup>1</sup> and Rosen,<sup>2</sup> the internuclear distances for the ground state have a relatively small value of 1.416 Å. This has been determined by Lowater,<sup>6</sup> and confirmed by Tanaka and Horie.<sup>7</sup> However, Herzberg<sup>1</sup> has noted that the internuclear distances are doubtful, and this is confirmed by Lagerqvist, Uhler, and Barrow.<sup>8</sup> They have considered the ground state to be  $^3\Delta$  with  $r_e = 1.728$  Å. Other data they obtained are summarized in table 81. They have also found the dissociation energy of the ground state ( $^3\Delta$ ) to be 8.4 e. u.

TABLE 81

ROTATIONAL CONSTANTS BY LAGERQVIST et al<sup>8</sup>

State	$B_0$ (cm <sup>-1</sup> )	$D_0$ (cm <sup>-1</sup> )	$r_e$ (10 <sup>-8</sup> cm)
$C^3\Delta$	0.3927	$0.26 \times 10^{-6}$	1.775
$A^3\phi$	0.4035	$0.33 \times 10^{-6}$	1.752
$X^3\Delta$	0.4146	$0.32 \times 10^{-6}$	1.728

Further confirmation of the rotational analysis by Lagerqvist et al<sup>8</sup> is shown by the work of Murthy.<sup>9</sup> He has studied the intensity of the  $\alpha$  (C-X) band system and obtained internuclear distances in agreement with Lagerqvist et al.<sup>8</sup>

Uhler and Akerlind<sup>4</sup> have studied the singlet system  $A^*$  for ZrO (1956). They have considered it likely that this system corresponds to  $^1\Sigma - ^1\Sigma$  transition but consider it possible to be a  $^1\Delta - ^1\Delta$  transition. The first possibility of the  $^1\Sigma - ^1\Sigma$  transition would be in agreement with Afaf's<sup>3</sup> interpretation regarding a  $b^1\Sigma - a^1\Sigma$  transition. Uhler and Akerlind further indicate that the problem of the ground state of ZrO is still not determined. For the lower state ( $a^1\Sigma$  or possibly  $^1\Delta$ ), they find  $B_e = 0.4241$  cm<sup>-1</sup> and  $r_e = 1.711$  Å. Akerlind<sup>5</sup> has investigated the singlet system B and considers it to be either a  $^1\Sigma - ^1\Sigma$  or a  $^1\Delta - ^1\Delta$  transition. He labels the upper state d and the lower state c, in distinction to the  $C^1\Sigma$  and  $b^1\Sigma$  states found by Afaf<sup>3</sup> ( $b^1\Sigma$  is upper state) for the singlet system B\*. Akerlind<sup>5</sup> further notes that the  $X^3\Delta$  and  $a^1\Sigma$  states are expected to be close to each other.

For the  $\beta$ -system  $B^3\Pi - X^3\Delta$  of ZrO, Uhler<sup>10</sup> has performed a rotational analysis. Uhler shows that the ground state is  $X^3\Delta$  and obtains  $B_0 = 0.4145$  cm<sup>-1</sup>,  $D_0 = 0.30 \times 10^{-6}$  cm<sup>-1</sup>, and  $r_e = 1.728 \times 10^{-8}$  cm. These values are in excellent agreement with the data of Lagerqvist, Uhler, and Barrow<sup>8</sup> given in table 81.

\*See table 80.

From Herzberg<sup>1</sup> (p. 108), a formula for rotational constant is given; i. e.,

$$B_v = B_e - a_e \left( v + \frac{1}{2} \right) + \gamma_e \left( v + \frac{1}{2} \right)^2 + \dots$$

Therefore, if the squared term is neglected,

$$B_v = B_e - a_e \left( v + \frac{1}{2} \right) + \dots, \text{ and letting } v = 0, B_0 = B_e - a_e \left( \frac{1}{2} \right);$$

that is,

$$B_e = B_0 + a_e \frac{1}{2}$$

Hence using the values of Lagerqvist, Uhler, and Barrow<sup>8</sup> for  $B_0$  and  $a$  of the  $X^3\Delta$  state,

$$B_e = 0.4146 + \frac{1}{2} (0.0021),$$

$$B_e = 0.4156 \text{ cm}^{-1}$$

are obtained.

This calculated value for  $B_e$  is accepted for the ground state in the present calculations.

In table 82, the spectroscopic constants adopted are presented. Because of the possibility of other low-lying electronic states, no attempt is made to include levels above the  $c^1\Sigma$  state. Vibrational constants are from Rosen.<sup>2</sup> The term values for the  $\Sigma$  state from Rosen<sup>2</sup> have been converted to  $\nu_{00}$  values (i. e., energy level above the ground-state vibrational level) by the relation from Herzberg<sup>1</sup> (p. 152).

$$\nu_{00} = \nu_e + \frac{1}{2} \omega_e' - \frac{1}{4} \omega_e x_e' - \frac{1}{2} \omega_e'' + \frac{1}{4} \omega_e x_e''$$

where the primes refer to the upper states, and the double primes refer to the lower states. For  $T_e = \nu_e = 1300 \text{ cm}^{-1}$ ,

$$\begin{aligned} \nu_{00} &= 1300 + \left( \frac{1}{2} \times 978.07 - \frac{1}{4} (5.04) \right) - \frac{1}{2} (936.5) + \frac{1}{4} (3.47) \\ &= 1300 + 489.035 - 1.260 - 468.25 + 0.867 \end{aligned}$$

$$\nu_{00} = 1320.3 \text{ cm}^{-1}.$$

TABLE 82

SPECTROSCOPIC CONSTANTS USED IN CALCULATIONS FOR  
ZIRCONIUM MONOXIDE (gas)  
(All Quantities in  $\text{cm}^{-1}$ )

State	$g^\circ$	E	$\omega_e$	$\omega_e x_e$	$B_e$	$a_e$	$\gamma_e$	$D_e$
$c^1\Sigma$	1	9171.2	938.1	1.80	0.3951**	0.0019**	-	$0.35 \times 10^{-6}$ **
$a^1\Sigma$	1	1320.3	978.07	5.04	0.4241**	0.0023**	-	$0.33 \times 10^{-6}$ **
$x^3\Delta$	2	605.1						
	2	297.2	936.5	3.47	0.4156***	0.0021***	-	$0.32 \times 10^{-6}$ ***
	2	0						

\* Dimensionless.

\*\* Data from Uhler and Akerlind.<sup>4</sup>

\*\*\* Data from Lagerqvist, Uhler, and Barrow.<sup>8</sup>

For  $T_e = \nu_e = 9170$ ,

$$\nu_{00} = 9170 + \left(\frac{1}{2} \times 938.1 - \frac{1}{4}(1.80)\right) - \left(\frac{1}{2}(936.5) - \frac{1}{4}(3.47)\right)$$

$$\nu_{00} = 9171.21 \text{ cm}^{-1} = 9170. + 469.05 - 0.45 - 468.25 + 0.867.$$

Thermodynamic functions including heat capacity, entropy, free-energy functions, and enthalpy content have been calculated using the diatomic gas computer program with the input data of table 82.

#### b. Heat of Formation

Ackermann and Thorn<sup>11</sup> have accepted a dissociation energy of 7.8 e.v. (179.891 kcal/mole) for  $\text{ZrO}$  in agreement with Herzberg<sup>1</sup> and Chupka, Berkowitz, and Inghram.<sup>12</sup> Nakata, McKisson, and Pollock<sup>13</sup> have made vaporization studies of zirconium dioxide and also obtained a dissociation energy of 7.8 e.v. Additional vaporization studies for the  $\text{ZrO}_2$  system have been reported by Ackermann and Thorn,<sup>14</sup> Hoch, Nakata, and Johnston,<sup>15</sup> Alexander and Ogden,<sup>16</sup> and Wolff and Alcock.<sup>17</sup> JANAF tables<sup>18</sup> have adopted a heat of dissociation of  $D_0 = 183 \pm 5$  kcal/mole and a heat of formation of  $\Delta H_{f298.15}^\circ = 21.1 \pm 5$  kcal/mole.

From spectroscopic studies, Lagerqvist, Uhler, and Barrow<sup>8</sup> have found the dissociation energy to be 8.4 e.v. (193.729 kcal/mole).

Lagerqvist et al<sup>8</sup> have used the formula  $D_e = \frac{\omega_e^2}{4\omega_e x_e}$  to evaluate the dissociation energy of the  $X^3\Delta$ ,  $A^3\Phi$ , and  $C^3\Delta$  states. The mean result for the ground state is 8.4 e.v. However, they indicate that their method of calculation usually gives too high a value. Thus, it would appear that lower values are most likely.

A thorough analysis of the vaporization data could not be performed at the time of report preparation. Accordingly, an interim choice of  $\Delta H_{f298.15}^\circ = 21.1$  kcal/mole has been accepted as the heat of formation for  $ZrO_{(g)}$  based on the JANAF tables. Thus, the resultant table is to be considered subject to revision.

### c. Uncertainties

Because of the possibility of unobserved, low-lying electronic states in the  $ZrO$  molecule, it is likely that the functions calculated, such as heat capacity, entropy, free-energy functions, and enthalpy, may be subject to appreciable errors. To give a possible indication of the uncertainties, calculations of the various thermodynamic functions have been made using different possible inputs.

Brewer and Chandrasekharaiah<sup>19</sup> have utilized a procedure to estimate the electronic contribution to free-energy functions by using a simple ionic model. Thus, they assume that electronic energy levels of the molecular species can be estimated from the known energy levels of the corresponding metal ion having a +2 charge. Effectively, they assume that the approach of an oxide ion causes no appreciable perturbation of the energy levels. Reference to Moore's table<sup>20</sup> give the following low-lying energy levels for  $Zr^{+2}$  in table 83. Additional higher states are here neglected.

TABLE 83  
ENERGY LEVELS FOR ZIRCONIUM<sup>+2</sup> ION

Designation	J	Level (cm <sup>-1</sup> )
$a^3F$	2	0.0
	3	681.
	4	1486.4
$a^1D$	2	5741.55
$a^3P$	0	8062.07
	1	8325.65
	2	8838.21

Two methods of computing the data have been used. In the first (HS69), all the energy levels from table 84 have been used; whereas, for the second (HS70), only the first two electronic states have been used. The actual data used in calculations are shown in table 84.

TABLE 84

DATA USED IN CALCULATING FUNCTIONS FOR ZIRCONIUM  
MONOXIDE ( gas ) BY DIFFERENT APPROXIMATIONS OF  
ELECTRONIC ENERGY LEVELS

Case HS69 - Three electronic states

$g$	$E$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )
5.0	0.0	936.5	0.4147
7.0	681.	936.5	0.4147
9.0	1486.4	936.5	0.4147
5.0	5741.55	936.5	0.4147
1.0	8062.07	936.5	0.4147
3.0	8325.65	936.5	0.4147
5.0	8838.21	936.5	0.4147

Case HS70 - Two electronic states

$g$	$E$ ( $\text{cm}^{-1}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )
5.0	0.0	936.5	0.4147
7.0	681.	936.5	0.4147
9.0	1486.4	936.5	0.4147
5.0	5741.55	936.5	0.4147

In table 84, the vibrational frequencies have been considered equal in all states and are given the same value tabulated by Brewer and Chandrasekaraiah.<sup>19</sup> Similarly, the rotational constant  $B_e$  is calculated from the internuclear distance 1.728 Å tabulated by the same authors.



In table 85, data at 298.15, 1000°, 2000°, 3000°, 4000°, 5000°, and 6000°K have been presented for the various cases considered. In addition to the two cases already cited (i. e., HS69 and HS70), data for the accepted tables of this report (HS72) and from the JANAF table<sup>18</sup> are also listed. It is seen that significant differences can arise, and these differences are used as a guide in the estimation of the uncertainties.

It is of interest to compare the resultant free-energy functions with those tabulated by Brewer and Chandrasekharaiah. They have found

$$-\frac{F_T^\circ - H_o^\circ}{T}_{298.15} = 50.6 \text{ e.u.}$$

and

$$-\left(\frac{F_T^\circ - H_o^\circ}{T}\right)_{3000} = 70.6 \text{ e.u.}$$

since

$$-\frac{F_T^\circ - H_o^\circ}{T} = -\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right) - \left(\frac{H_{298}^\circ - H_o^\circ}{T}\right)$$

Then for case HS69 at 298°K,

$$H_{298}^\circ - H_o^\circ = 2,205 \text{ cal/mole and } -\frac{F_T^\circ - H_{298}^\circ}{T} = 58.029 \text{ e.u.}$$

Therefore,

$$\begin{aligned} -\left(\frac{F_T^\circ - H_o^\circ}{T}\right)_{298.15} &= 58.029 - \frac{2205}{298.15} \\ -\frac{F_T^\circ - H_o^\circ}{T}_{298.15} &= 50.634 \text{ e.u.} \end{aligned}$$

At 3000°K,

$$-\frac{F_T^\circ - H_o^\circ}{T}_{3000^\circ\text{K}} = 71.493 - \frac{2205}{3000} = 70.758 \text{ e.u.}$$

TABLE 85

COMPARISON OF VARIOUS SOURCES OF DATA FOR  
ZIRCONIUM MONOXIDE (gas)

T °K	Case	$C_p^\circ$	$S_T^\circ$	$\left(\frac{F_T^\circ - H_{298}^\circ}{T}\right)$	$H_T^\circ - H_{298}^\circ$ kcal gfw <sup>-1</sup>
cal deg K <sup>-1</sup> gfw <sup>-1</sup>					
298.15	HS69	8.548	58.029	58.029	0.000
298.15	HS70	8.548	58.029	58.029	0.000
298.15	HS72*	8.632	57.055	57.055	0.000
298.15	JANAF	8.620	57.069	57.069	0.000
1000	HS69	9.755	69.625	62.825	6.800
1000	HS70	9.754	69.625	62.825	6.800
1000	HS72*	9.096	67.876	61.569	6.307
1000	JANAF	9.099	67.888	61.581	6.307
2000	HS69	9.492	76.258	68.081	16.355
2000	HS70	9.394	76.238	68.078	16.320
2000	HS72*	9.124	74.186	66.480	15.412
2000	JANAF	9.095	74.194	66.492	15.403
3000	HS69	9.581	80.123	71.493	25.891
3000	HS70	9.316	80.030	71.473	25.671
3000	HS72*	9.212	77.902	69.710	24.577
3000	JANAF	9.114	77.884	69.716	24.506
4000	HS69	9.604	82.885	74.012	35.491
4000	HS70	9.253	82.702	73.963	34.955
4000	HS72*	9.307	80.567	72.108	33.837
4000	JANAF	9.147	80.510	72.102	33.635
5000	HS69	9.559	85.024	76.009	45.076
5000	HS70	9.197	84.760	75.924	44.180
5000	HS72*	9.386	82.655	74.018	43.185
5000	JANAF	9.187	82.556	73.995	42.802
6000	HS69	9.489	86.761	77.661	54.601
6000	HS70	9.152	86.433	77.541	53.353
6000	HS72*	9.454	84.377	75.610	52.606
6000	JANAF	9.229	84.234	75.566	52.009

\* These data are used in the final accepted tables of  
present work.

Thus, the data from HS69 agree well with the values tabulated by Brewer and Chandrasekharaiah as expected.

At the present time, it is not clear how accurate are the thermodynamic functions calculated for  $ZrO_{(g)}$ . However, the range of values in table 85 is herein considered a possible guide to the uncertainties.

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### 35.4.2 Zirconium Dioxide ( $\text{ZrO}_2(\text{s}, \ell)$ )<sup>1</sup>

#### a. Phase Diagram, Crystal Structure, and Transition and Melting Points

The phase diagram given by Hansen and Anderko<sup>1</sup> for the Zr-O system shows the presence of a single compound, i. e.,  $\text{ZrO}_2$ . The possibility of other lower suboxides, such as  $\text{ZrO}$  and  $\text{Zr}_2\text{O}_3$ , has been postulated by some workers, but Hansen and Anderko<sup>1</sup> cite the work of Domagala and McPherson<sup>2</sup> and Cubicciotti<sup>3</sup> who could not find any evidence for such suboxides. Weber et al<sup>4</sup> also could not find a suboxide, and Hoch et al<sup>5</sup> have accepted the fact that suboxides do not exist. The latter authors show a slightly modified phase diagram for the Zr-O system. Brewer<sup>6</sup> also mentions the work of Brewer, Templeton, and McCullough,<sup>7</sup> which showed that no new phases could be detected upon heating Zr with  $\text{ZrO}_2$ . Brewer concludes that the lower oxides are unstable by disproportionation or, at best, only slightly stable.

For the present compilation, we accept the analysis of Hansen and Anderko<sup>1</sup> that  $\text{ZrO}_2$  is the only compound and restrict attention to the very refractory phase  $\text{ZrO}_2$ .

Hansen and Anderko<sup>1</sup> state that  $\text{ZrO}_2$  has two established crystalline modifications. At low-temperature, the monoclinic form is considered stable whereas, at high temperatures (above about  $1000^\circ\text{C}$ ), a tetragonal form is stable. Other forms, such as the well known cubic modification of  $\text{ZrO}_2$ , can only be formed when a stabilizing agent, such as  $\text{MgO}$ ,  $\text{CaO}$ , etc., are present as impurities. Hoch and Mathur<sup>8</sup> found that cubic  $\text{ZrO}_2$  can be formed from tetragonal  $\text{ZrO}_2$  and transition metals of groups V and VI, or their monoxides only if  $\text{TiO}_2$  is present. Weber<sup>9</sup> has pointed out many errors of the conflicting views regarding possible crystalline forms of  $\text{ZrO}_2$ , and further adds that "the problem of zirconium systems is highly complex." Weber feels that the question of the possible existence of a cubic structure of pure  $\text{ZrO}_2$  is still unsettled. Weber also questions the validity of determining phase transition by observing cracking of specimens as Lynch et al<sup>10</sup> have done.

In the present work, we accept the Hansen and Anderko<sup>1</sup> viewpoint that monoclinic  $\text{ZrO}_2$  is the stable low-temperature form and tetragonal  $\text{ZrO}_2$  is the stable high-temperature modification. Brewer<sup>6</sup> indicates the transition temperature to be  $1205^\circ\text{K}$ . This may possibly be a typographical error, i. e., it might be  $1205^\circ\text{C}$ , since Kelley<sup>11</sup> accepts a transition temperature of  $1478^\circ\text{K}$ . Similarly, Coughlin<sup>12</sup> and Coughlin and King<sup>13</sup> had accepted  $1478^\circ\text{K}$  as the transition temperature.

It is clear that there is a discrepancy in the temperature of transition however. Thus, Hansen and Anderko<sup>1</sup> quote several references to indicate the temperature of transition is about 1000°C (1273°K). Lynch, Vahldiek, and Robinson<sup>10</sup> found the transition to occur at 1193 to 1200°C (1466 to 1473°K). Additional comments on phase transformations for ZrO<sub>2</sub> have been made by Whitney,<sup>14</sup> Evans and Wildsmith,<sup>15</sup> Hinz and Dietzel,<sup>16</sup> Vahldiek, Robinson, and Lynch,<sup>17</sup> Garrett,<sup>18</sup> Ruh and Simmons,<sup>19</sup> and Mumpton and Roy.<sup>20</sup> The last authors found a transition temperature of 1170°C (1443°K) by differential thermal analysis. They found this temperature to be raised to 1190°C (1463°K) for "natural" ZrO<sub>2</sub> which contains 2 percent HfO<sub>2</sub>. Curtis, Doney, and Johnson<sup>21</sup> found by differential thermal analysis that the maximum endothermic reaction occurred at 1190°C (1463°K).

For the present work, we accept the transition temperature used by Kelley<sup>11</sup> and Coughlin et al;<sup>12, 13</sup> i. e., 1478°K.

A range of values for the melting point of ZrO<sub>2</sub> has been reported. Thus, Hansen and Anderko<sup>1</sup> list values of 2677, 2687, 2715, and 2710°C to give an average value of 2700°C (2973°K). Brewer<sup>6</sup> lists a value of 2960°K, and NBS<sup>22</sup> lists a value of 2950°K. Curtis, Doney, and Johnson<sup>21</sup> reported a relatively high melting point of 2850 ± 25°C (3123°K) for a hafnium-free sample of zirconia.

In the present work, we accept the average value as recorded by Hansen and Anderko for the melting point of 2973°K.

## b. Thermodynamic Properties

### 1) Low-temperature heat capacity and entropy at 298.15°K

Kelley<sup>23</sup> has reported low-temperature heat capacity measurements for the range 54.3 to 295.0°K. For the lower temperatures below his experimental points, he used the following sum of Debye and Einstein functions:

$$C_p^\circ = D \frac{345}{T} + E \frac{513}{T} + E \left( \frac{861}{T} \right)$$

Kelley reported  $S_{298.15}^\circ = 12.03 \pm 0.08 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ . He did not report a value of  $H_{298.15}^\circ - H_0^\circ$ . In the present work, we have performed the integration to 298.15°K, using  $C_p^\circ$ , 298.15°K from Kelley and King<sup>24</sup> who reported  $S_{298.15}^\circ = 12.12 \pm 0.08 \text{ e.u.}$  It was found that  $H_{54.0}^\circ - H_0^\circ = 0.022 \text{ kcal gfw}^{-1}$  and  $H_{298.15}^\circ - H_0^\circ = 2.091 \text{ kcal gfw}^{-1}$ . In the present tabulation, we accept the latest Kelley and King<sup>24</sup> value of  $S_{298.15}^\circ$  and our value of  $H_{298.15}^\circ - H_0^\circ$ .

## 2) High-temperature heat content

Kelley<sup>11</sup> has summarized high-temperature heat content measurement data prior to 1960. His work includes the Coughlin and King<sup>13</sup> data which covered the range 298.15 to 1841°K. The enthalpy data could be represented to a precision of 0.2 percent in the range 298 to 1478°K, giving as an equation:

$$C_p^\circ = 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^{-5}T^2 \quad \text{cal deg K}^{-1} \text{ gfw}^{-1}.$$

At 1478°K, a transition from monoclinic to tetragonal ZrO<sub>2</sub> with a heat effect of 1420 cal deg K<sup>-1</sup> gfw<sup>-1</sup> is considered.

Above 1478°K, the enthalpy could be represented to an accuracy of 0.1 percent by assuming  $C_p^\circ = 17.80 \text{ cal deg K}^{-1} \text{ gfw}^{-1}$ .

More recent work has been reported by Victor and Douglas<sup>25</sup> for the range 0 to 900°C and by Pears et al<sup>26</sup> for the range 690 to 4505°F (638.7 to 2758.1°K). The enthalpy values found by Pears et al<sup>26</sup> have been converted to cgs units and referred to 298.15°K by using the correction  $H_{298.15}^\circ - H_{273.15}^\circ = 0.327 \text{ kcal gfw}^{-1}$  from the integration of low-temperature data mentioned in the previous section. The converted data are shown on the following page.

Comparison of the enthalpy value obtained by Pears et al with those from Kelley<sup>11</sup> indicated that up to 2000°K the Pears et al<sup>26</sup> data are too large by up to 2.5 kcal gfw<sup>-1</sup>. At higher temperatures, even larger deviations occur. It may be also noted that Pears et al<sup>26</sup> (p. 123) show a plot of  $C_p^\circ$  for a sample of ZrO<sub>2</sub> containing 4 percent CaO which agrees much better with the Kelley<sup>11</sup> data than the data they actually reported. In view of these facts, it appears best to accept the Kelley<sup>11</sup> data. The Victor and Douglas<sup>25</sup> data are not given any weight, since its temperature range did not span the transition temperature, and because of the good internal consistency of the Kelley data. Accordingly, we have extrapolated the Kelley equation to a temperature selected, for convenience, as 2000°K. From this temperature to the chosen melting point, it was assumed that  $C_p^\circ$  varies linearly from 17.8 to 24.0, i. e.,  $C_p^\circ = 5.056 + 0.006372T \text{ cal deg K}^{-1} \text{ gfw}^{-1}$  was assumed from 2000 to 2973°K. The heat of fusion was estimated to be 25.0 kcal gfw<sup>-1</sup>; and the heat capacity of liquid ZrO<sub>2</sub> was considered to be 24.0 cal deg K<sup>-1</sup> gfw<sup>-1</sup>.

## 3) Heat of formation

Humphrey<sup>27</sup> used oxygen-bomb calorimetry to produce monoclinic ZrO<sub>2</sub> and found that  $\Delta H_{f,298.15}^\circ = -261.5 \pm 0.2 \text{ kcal gfw}^{-1}$ . He

ENTHALPY DATA FOR  $\text{ZrO}_2$  FROM PEARS et al<sup>26</sup>

T (°K)	$H_T^\circ - H_{298.15}^\circ$ (cal gfw <sup>-1</sup> )
638.7	6189.9
1058.7	14733.2
1292.0	18635.1
1674.8	26678.6
1952.5	33147.7
2185.9	38350.3
2238.7	39787.9
2355.3	43614.5
2536.3	49782.4
2758.1	58455.7



used an atomic weight of  $\text{Zr} = 91.22$  and  $\text{O} = 16.00$ , in accord with the values used in the present tabulation. As noted many times heretofore, the present tabulation, for purposes of consistency, has not yet converted to the newer 1961 atomic weights, but used the chemical scale of atomic weights accepted prior to 1961. It should be noted, however, that the differences are essentially insignificant.<sup>28</sup>

Earlier data reviewed by the National Bureau of Standards<sup>22</sup> indicated a heat of formation for  $\text{ZrO}_2$  at  $298.15^\circ\text{K}$  of  $-258.2 \text{ kcal/gfw}$ . This included works by Neumann, Kröger and Kunz<sup>29</sup> ( $-258.2 \text{ kcal gfw}^{-1}$ ), Roth, Borger, and Siemonsen<sup>30</sup> ( $-258.8 \text{ kcal gfw}^{-1}$ ), Roth and Becker<sup>31</sup> ( $-258.1 \text{ kcal gfw}^{-1}$ ), and Weiss and Neumann.<sup>32</sup>

Kubaschewski and Evans<sup>33</sup> selected a heat of formation of  $-259.2 \pm 1.2 \text{ kcal gfw}^{-1}$ , and Brewer<sup>34</sup> chose a value of  $-261.8 \text{ kcal gfw}^{-1}$ . This latter value was attributed to Kelley and, hence, is undoubtedly a preliminary value of the data reported by Humphrey.

Kubaschewski and Catterall<sup>35</sup> have analyzed all of the reported work and chose  $-259.5 \text{ kcal gfw}^{-1}$  as the heat of formation. Kubaschewski and Dench<sup>36</sup> have measured dissociation pressures in the zirconium-oxygen system at  $1000^\circ\text{C}$ . Lilliendahl, Gregory, and Wroughton<sup>37</sup> also measured the oxygen content of  $\beta$ -zirconium in equilibrium with  $\text{CaO}$  and  $\text{Ca}$  at  $1000$  and  $1300^\circ\text{C}$ . Komarek and Silver<sup>38</sup> reported similar data more recently for the range  $1100^\circ$  to  $1300^\circ\text{K}$ , and  $0$  to  $30$  atom-percent oxygen. Such data, if accurate and covering a sufficient range of composition, can be used to derive integral free energies of formation and, subsequently, heats of formation. Unfortunately, in the present case, the data do not cover the complete range of  $x = 0$  to  $2$  in the formula  $\text{ZrO}_x$ . Thus, the data of Komarek and Silver cover the composition range of oxygen from  $0$  to  $29$  atom percent ( $x = 0$  to  $0.41$ ). From  $29$  atom percent to  $65$  atom percent ( $x = 0.41$  to  $1.857$ ) via the phase diagram of Hansen and Anderko, a two-phase field  $\alpha\text{-Zr} + \text{ZrO}_{1.857}$  exists at  $1273^\circ\text{K}$ . In this range, the relative partial molar free energy of oxygen  $\bar{\Delta F}_{\text{O}_2}$  is constant and equal to the value  $\bar{\Delta F}_{\text{O}_2}$

at  $x = 0.41$ . However, for the homogeneity range  $\text{ZrO}_{1.857}$  to  $\text{ZrO}_2$ , there are only limited data for  $\bar{\Delta F}_{\text{O}_2}$ . Aronson<sup>39</sup> gives data near the  $\text{ZrO}_2$  limit.

Herein, it was felt that use of the calorimetric data would yield more accurate free-energy data than using the somewhat incomplete data on oxygen dissociation pressures.

In the present work, the calorimetric determination given by Humphrey<sup>27</sup> is accepted, since his sample contained purer Zr than was available to earlier workers. Thus, we accept  $\Delta H_f^{298.15} = -261.5 \text{ kcal gfw}^{-1}$ . It appears possible that this number might be subject to an uncertainty of, perhaps, 1 or 2 kcal gfw<sup>-1</sup>. It has been noted by Huber and Holley<sup>40</sup> that this value is still unconfirmed.

#### 4) Vaporization studies

Chupka, Berkowitz and Inghram<sup>41</sup> have used a mass spectrometer to study the vaporization of ZrO<sub>2</sub>. They observed both ZrO(g) and ZrO<sub>2</sub>(g). Nakata, McKisson, and Pollock<sup>42</sup> used Knudsen effusion in the range 2410° to 2830°K. They utilized mass spectrometer observations to estimate the composition of the vapor. Ackermann and Thorn<sup>43</sup> have reviewed much of the earlier vaporization work, including their own. They noted that the work of Hoch *et al*<sup>44</sup> suffered from failure to consider the presence of gaseous tantalum oxides. Ackermann and Thorn<sup>43</sup> have mentioned that the residual phase from Knudsen effusion was ZrO<sub>1.97</sub>. Nakata *et al*<sup>42</sup> have attributed other presumably more recent work to Ackermann and Thorn<sup>45</sup> for which congruent vaporization and a minimum volatility occur at ZrO<sub>1.96</sub>. For this composition, ZrO(g) is the predominant species.

Further discussion of vaporization data may be found in the sections devoted to ZrO(g) and ZrO<sub>2</sub>(g).

#### Supplement

Vahldiek, Robinson, and Lynch<sup>46</sup> have recently discussed the preparation of tetragonal ZrO<sub>2</sub> at 15 to 20 kb and 1200° to 1700°C. The sample when heated to 1200°C in air reverted to the monoclinic form. This is expected from the thermodynamic analysis of Whitney.<sup>14</sup> Other recent work on the monoclinic-tetragonal transition has been given by Baun,<sup>47</sup> and Wolten.<sup>48</sup> Wolten finds the monoclinic-tetragonal phase change to resemble a martensitic phase transformation with a hysteresis loop. He also confirmed the reversible formation of cubic ZrO<sub>2</sub> above 2200°C in agreement with Smith and Cline.<sup>49</sup>

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\*kb is abbreviation for kilobars.

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### 35.4.3 Zirconium Dioxide ( $\text{ZrO}_2(\text{g})$ )

#### Thermodynamic Functions

Because there are no available experimental data for the spectroscopic constants of  $\text{ZrO}_2(\text{g})$ , it has been necessary to make assumptions regarding the structure of this molecule.

Brewer and Rosenblatt<sup>1</sup> assumed  $\text{ZrO}_2$  to be a linear molecule and computed free energy functions at 500°K intervals. They did not list their vibrational frequencies obtained, but earlier, using similar calculations, Chandrasekharaiah and Brewer<sup>2</sup> found:

$$\omega_1 = 863 \text{ cm}^{-1} \quad (\text{multiplicity} = 1)$$

$$\omega_2 = 260 \text{ cm}^{-1} \quad (\text{multiplicity} = 2)$$

$$\omega_3 = 1000 \text{ cm}^{-1} \quad (\text{multiplicity} = 1).$$

JANAF<sup>3</sup> used the structural data estimated by Chupka et al.<sup>4</sup> These data included:

$$\omega_1 = 865 \text{ cm}^{-1} \quad (\text{multiplicity} = 1)$$

$$\omega_2 = 271 \text{ cm}^{-1} \quad (\text{multiplicity} = 2)$$

$$\omega_3 = 1003 \text{ cm}^{-1} \quad (\text{multiplicity} = 1)$$

$$\text{and } I = 15.865 \times 10^{-39} \text{ g cm}^2.$$

In the present work, assumptions rather similar to those of Brewer and Rosenblatt<sup>1</sup> were used. The valence-bond approximation was thus used to estimate vibrational frequencies for the assumed linear molecule. An interatomic distance of 1.728Å based on the value for the monoxide from Sutton<sup>5</sup> was used. The results obtained are tabulated on the following page:

TABLE 86

DATA ESTIMATED BY VALENCE-BOND METHOD FOR  $\text{ZrO}_{2(g)}$ 

Force constant, stretching, $k$	$7.032 \times 10^5$	dyne/cm
Force constant, bending, $k_\delta/l^2$	$2.391 \times 10^4$	dyne/cm
Rotational constant, $B_e$	0.17643	$\text{cm}^{-1}$
$\omega_1$	863.8	$\text{cm}^{-1}$
$\omega_2$ (doubly degenerate)	261.8	$\text{cm}^{-1}$
$\omega_3$	1003.9	$\text{cm}^{-1}$
Symmetry number, $\sigma$	2.	

Electronic contributions were assumed to be negligible, that is, it was assumed that the electronic ground state is  $1g$  with no other low electronic states. Moore<sup>6,7</sup> does not show energy levels for  $\text{Zr}^{+4}$ . However, for the analogous  $\text{Ti}^{+4}$  ion the next level above the ground state is  $436880 \text{ cm}^{-1}$ , i. e., it is unimportant. Thus, it is not expected that there will be any electronic contributions in the present case.

#### Heat of formation

Brewer and Rosenblatt<sup>1</sup> have recalculated the vaporization data of Chupka, Berkowitz, and Inghram<sup>4</sup> to give a second-law heat of sublimation of  $H_{298.15}^\circ = 179.6 \text{ kcal/mole}$  and a third-law heat of sublimation of  $H_{298.15}^\circ = 179.8 \text{ kcal/mole}$ . Using the average heat of sublimation  $179.7 \text{ kcal/mole}$ , together with the heat of formation for  $\text{ZrO}_2$  of  $-261.5 \text{ kcal gfw}^{-1}$  by Humphrey,<sup>8</sup> the heat of formation of  $\text{ZrO}_2(g)$  is found to be

$$H_f^\circ, \text{ZrO}_2(g), 298.15 = -81.8 \text{ kcal/mole.}$$

In order to develop self-consistent functions, the vapor pressure data of Chupka et al<sup>4</sup> have been recomputed, using the third law. For this computation, free energy functions for  $\text{ZrO}_2(\text{cond})$  were obtained from the present work. The results of the calculations are shown in table 87.

From the average heat of sublimation  $\Delta H_{298.15}^\circ = 179.043$  kcal gfw<sup>-1</sup> found in table 87, we can now calculate the heat of formation of  $\text{ZrO}_2(\text{g})$ , using the value of the heat of formation of  $\text{ZrO}_2(\text{solid}) = -261.5$  kcal gfw<sup>-1</sup> accepted in the present work and based on Humphrey's data.<sup>8</sup> Thus, the heat of formation of  $\text{ZrO}_2(\text{g})$  is given as:

$$\begin{aligned}\Delta H_{298.15, \text{ZrO}_2(\text{g})}^\circ &= -261.5 + 179.043 \\ &= -82.457 \text{ kcal gfw}^{-1}.\end{aligned}$$

TABLE 87

VAPORIZATION DATA FOR  $\text{ZrO}_2$  ACCORDING TO THE REACTION  
 $\text{ZrO}_2(\text{solid}) \longrightarrow \text{ZrO}_2(\text{gas})$

T (°K)	P <sub>ZrO<sub>2</sub></sub> (atm)	$\frac{F_T^\circ - H_{298}^\circ}{T}$ $\text{ZrO}_2(\text{solid})$ (cal deg K <sup>-1</sup> gfw <sup>-1</sup> )	$\frac{F_T^\circ - H_{298}^\circ}{T}$ $\text{ZrO}_2(\text{gas})$ (cal deg K <sup>-1</sup> gfw <sup>-1</sup> )	$\Delta H_{298.15}^\circ$ (kcal gfw <sup>-1</sup> )
2421	$6.9 \times 10^{-8}$	32.791	74.838	181.127
2480	$5.9 \times 10^{-8}$	33.185	75.139	186.083
2416	$4.8 \times 10^{-8}$	32.758	74.812	182.514
2331	$3.6 \times 10^{-8}$	32.178	74.367	177.739
2340	$2.1 \times 10^{-7}$	32.240	74.415	170.191
2471	$1.4 \times 10^{-7}$	33.125	75.093	181.199
2374	$1.4 \times 10^{-7}$	32.473	74.594	174.448
Average				179.043

From the accepted heat of formation at 298.15°K, the heat of formation of  $\text{ZrO}_2(\text{g})$  at 0°K is found to be -81.794 kcal gfw<sup>-1</sup>. This leads to a heat of dissociation of 342.576 kcal gfw<sup>-1</sup> or 14.854 ev. Brewer and Rosenblatt<sup>1</sup> had calculated a heat of dissociation of  $347 \pm 5$  kcal at 298.15°K. Ackermann and Thorn<sup>9</sup> obtained values of 15.2 - 15.3 ev, and Nakata et al<sup>10</sup> obtained  $14.9 \pm 0.2$  ev in good agreement with the present calculations.



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## V. THE NEED FOR ORGANIZED EFFORTS

### A. Need for Critical Compilations

This work is neither a beginning nor an end. References to earlier compilations have been cited in many portions of this work. Furthermore, the supplements to the discussion section (section IV) show that many new references have become available even before the present work has been published. It is anticipated that continued interest in high temperatures will result in much new data in the near and more distant future. With this constant flow of new data, it is necessary that the data be analyzed as soon as possible, so that the most precise data will become generally available in a compilation.

The need for critical compilations of thermodynamic data has been recognized at a meeting of the National Research Council Office of Critical Tables in March 1963.<sup>1</sup>

The new National Standard Reference Data Program under the auspices of the National Bureau of Standards should provide a good opportunity for development of excellent compilations of thermodynamic data. By development of standard formats, standard methods of presentations, and clearly defined areas of responsibility, excellent compilations should result. This effort is in very preliminary stages as mentioned by Walker,<sup>2</sup> and in an earlier announcement.<sup>3</sup>

Thus, it is necessary that continued efforts be made to prepare and/or revise compilations of the present type.

### B. Standardization

In addition to the need for critical compilations, there is a great need for standardization in methods of obtaining and presenting thermodynamic data. Walker<sup>2</sup> has noted recent advances in standardization of the temperature scale. He also notes that the National Research Council has established a Committee on High Temperature Chemical Phenomena under Prof. J. L. Margrave. This committee<sup>4</sup> is considering the formulation of standard practices for recording and reporting high-temperature data.

Intimately related with the problems of standardization are the problems of choices of physical constants and systems of units. Some aspects of the physical constants' problem are discussed in section IIC. It may be noted that the chemists and physicists have been able to resolve their differences and have adopted a single atomic weight scale in 1961. More

recent work has seen the recommendation of a standard set of physical constants by a National Academy of Sciences' National Research Council committee.<sup>5</sup> These encouraging results should point the way to further standardization.

One of the major unresolved problems which needs further consideration is that of a choice of units. The United States is subject to two sets of units;<sup>6</sup> i. e. , one system uses the centimeter, the gram, the second, and the centigrade (Celsius) degree. The second uses the foot-pound-second system with degrees Fahrenheit. The length-mass-time units of the first system are from the metric system,\* whereas the foot-pound-second system is often called the English or British system of units.

In the present work, there have been many cases where data reported in one system must be converted to the other. Although the conversions are not difficult, they are annoying. Furthermore, the usage of two types of units may lead to erroneous interpretations. For example, data which are reported merely as "X degrees" might mean X°F, X°C, X°K, X°R, or other units. It is clear that the problem of consolidating units is a difficult one. Engineers have generally adopted the foot-pound-second-degree-Fahrenheit system, whereas scientists generally prefer the centimeter-gram-second-degree-centigrade system, but there are many cases of interchangeable usage by both. Recent expressions favoring retaining the dual system of units have been made by Mayer,<sup>7</sup> whereas two comments in favor of the metric system have been made by Frost<sup>8</sup> and Weber.<sup>9</sup> An entire volume has been prepared by Naft and DeSola<sup>10</sup> devoted to converting units used by various countries. It is noted that the Soviet Union is introducing the metric system.

Although the discussion over the relative merits of the dual system of units has been a long one (i. e. , it has been discussed for many decades in the United States), it is felt that efforts should be continued to consolidate the units. Emphasis should first be devoted to getting all thermochemical data reported in one set of units, but this problem is interwoven with the national and international one of different units. It is believed that if the chemists and physicists could resolve their difficulties, in adopting a unified atomic weight scale, that the same results could be obtained by serious discussions among engineers and scientists. To achieve such an objective may require considerable effort, but the gains would extend far beyond the realm of thermodynamics. It is probable that the achievement of a single system of units on an international scale would require a massive effort, including education at all levels of the populace of the United States and abroad, discussions in scientific and engineering societies, and finally recommendations by committees representing international organizations, government, industry, universities, engineering, and science.

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\*Most discussions of the metric system include only mass and length.

Thus, it is recommended that efforts be made to have all thermodynamic data reported in a single system of units. The much more difficult problem of adoption of a single set of units by all countries should also be considered.

More closely related to the areas of thermochemistry and thermodynamics is the need for standard methods of reporting data. Too often, scientists obscure their basic measured quantities by reporting only a derived quantity. Unless the intermediate data are reported, it becomes impossible to check the experimenter's calculations. In other cases, one scientist may tabulate his data, whereas another may give only a plot for the same kind of data. In the second case, there is not a precise value available to the user, but only one which can be interpolated from the graph. In many other aspects of scientific papers, it is clear that more standardization of presentation may be desirable. The sections devoted to material characterization should present an accurate description of the material used. Percentages by weight, by volume, by mole percent, etc., must be distinguished.

In making recommendations as to the best procedure for reporting data, it is suggested that the lead of recognized bodies, such as IUPAC,<sup>11</sup> the Calorimetry Conference,<sup>12</sup> various committees,<sup>1, 4</sup> and scientific journals, be followed. It is desirable that their suggestions then be consolidated and made generally available to all scientists.

#### C. Publication Means

The great increase in thermodynamic data, and the wide variety of journals in which data may be found, suggest that there may be need for a national or international journal devoted primarily to chemical thermodynamics and thermochemistry. Such a journal could help to develop some of the standard procedures and formats already advocated. Hence, consistent methods of presentation of data, units, formats, etc., could be developed. Furthermore, such a journal might be able to achieve and maintain an up-to-date survey of recently published thermodynamic data.

#### D. Materials Research and Materials Bank

Modern-day interest in high-temperature materials covers a variety of different outlooks varying from applied to basic research. Industrial organizations, Government agencies such as NASA and the Air Force, university groups, and international organizations all have a vital interest in high-temperature materials. Some recent references to modern-day research in high-temperature materials have been made.<sup>13-17</sup> Many other references to high-temperature work can be found in this compilation.

During the course of this work, the necessity of well characterized materials to form the basis of measurement programs has been amply demonstrated. Knowledge of the composition of a sample, its crystal structure, and many other related properties is needed, so that one can intelligently proceed to assign a certain value to a given physical property of a specified compound. Too often, data reported in the literature have been ascribed to one compound, whereas in reality some other compound has actually been studied.

Because of the high cost of research, and because of the time involved in preparing and analyzing high-quality material samples, it would appear appropriate that some single agency establish a materials bank. This bank could then maintain a supply of the highest-quality materials and supply samples to researchers who have a need for such materials. Several aspects of this problem have been discussed at an informal meeting called by Dr. H. M. Burte of the Air Force Materials Laboratory at the Asilomar Conference.<sup>14</sup> The National Research Council Committee on High Temperature Chemical Phenomena under the chairmanship of Prof. J. L. Margrave<sup>4, 18</sup> is also interested in the materials bank. Earlier work in this direction has been discussed by Kurtz<sup>19</sup> and Waddington.<sup>20</sup>

Closely related to the materials bank is the materials library. The object of a library would be to store material samples used by researchers in their studies. By having these samples stored in a "library," later investigators would have the opportunity to examine the material and perhaps explain discrepancies in experimental data.

It may be difficult to achieve a large-scale materials bank and materials library, but it is certainly worthy of continued thought. Perhaps, a modest beginning can lay the basis for a national or international bank of high-quality materials.

#### E. Education

This work has also illustrated the need for a wide variety of background information to understand and interpret high-temperature chemical phenomena. It is felt that educational institutions should strive to make their students familiar with a broad variety of disciplines as well as specialists in only a few of them. Perhaps, some of the older concepts in basic freshman college chemistry need to be revised, so that the atmosphere is clear and the student is in an attitude to accept such concepts as nonstoichiometric compounds. In addition to the concern for the new student, perhaps procedures should be developed for providing "refresher courses" to scientists whose formal education is completed.

Any or all of these proposals may lead to the desired goal of a higher quality and a higher quantity of research output.

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## VI. RECOMMENDATIONS FOR FURTHER WORK

### A. General

The present compilation has uncovered countless areas for which data are nonexistent. In many other areas, there have only been token efforts; and even in areas which have been well studied, there are often unexplainable contradictions. Many specific problem areas are indicated in the discussions of section IV. Here, only general problem areas will be discussed. It should be noted that thermodynamic data can be assigned greater dependability when verified by various investigators and by various techniques.

### B. Phase Data

Although there have been many reported studies of binary-phase diagrams (often in excellent agreement), it is clear that there is still a need for more precise information. Often, published phase diagrams have included data which might not represent true equilibrium. Hultgren *et al*<sup>1</sup> have commented on the disappointing accuracy of most phase diagrams. They also note that solidus curves determined from cooling curves are often too low in temperature because of segregation during cooling.

Many of the more well known phases have been thoroughly characterized and confirmed. However, there continue to be new reports of new compounds such as the suboxides. For example, Kornilov and Glazova<sup>2</sup> reported suboxides of  $Ti_6O$  and  $Ti_3O$ , whereas Hansen and Anderko's<sup>3</sup> phase diagram does not show any suboxide phase near these compositions. In the niobium-oxygen system, there have been reports of such suboxide phases as  $Nb_2O$ ,  $Nb_6O$ ,  $NbO_x$ , and  $NbO_z$ . Recent studies by Norman *et al*,<sup>4</sup> and Brauer *et al*,<sup>5</sup> discuss such work, but as yet the stable phases do not seem definitely known or confirmed. It is thus seen that the knowledge of phase data for such thoroughly studied systems as the oxides is still incomplete. In the cases of the borides, carbides, and nitrides, which have received even less study than the oxides, it is clear that much more work remains to be done.

In the case of the nitrides, it may be noted that for the Ti-N system; e. g., Hansen and Anderko<sup>3</sup> considered an  $\epsilon$ -phase and the TiN phase as the important ones. The  $\epsilon$ -phase has not been characterized with any degree of certainty. More recent work by Nowotny *et al*,<sup>6</sup> and Holmberg,<sup>7</sup> suggests that this phase is actually a  $Ti_2N$  phase. A similar report of an  $Hf_2N$  phase by Rudy and Benesovský<sup>8</sup> might then lead one to predict a  $Zr_2N$  phase in the Zr-N system. As yet, a  $Zr_2N$  phase has not been reported. On the other hand, there is the possibility that the subnitrides,  $Ti_2N$  and  $Hf_2N$ , are not true equilibrium phases.



In the case of the Ti-C system, one may note that heretofore only the TiC phase has been considered important. However, Raman and Ramachandran<sup>9</sup> recently reported finding a new bicarbide; i. e., TiC<sub>2</sub>. Although the formation of such a compound may be surprising, ultimately its existence must be confirmed or disproved.

For the borides, which in general have the greatest variety of reported compounds; e. g., formulas may range from Me<sub>2</sub>B to MeB<sub>12</sub> or higher, it is likely that even more surprises may be in store when the systems are studied in further detail.

Thus far, we have only tried to present some of the problems facing those who prepare phase diagrams. The examples are not meant to be comprehensive, but only to illustrate the fact that not even the possible compounds are definitely known for fairly well studied systems. It seems probable that a large portion of the tabulated phase diagrams may ultimately need varying degrees of revision.

If the possible compounds themselves are still not known in many binary-phase diagrams, it should be expected that other information is also in need of revision. Considering the modern-day interest in high-temperature materials, it is surprising to note that the only reported melting points for many refractories are taken from work in the 1920's and early 1930's by such pioneers as Agte and co-workers,<sup>10, 11</sup> and Friederich and Sittig.<sup>12</sup> Without casting any reflection on the excellent work of these men, it would still seem appropriate that modern redeterminations of these properties are required together with appropriate chemical analyses. Schneider<sup>13</sup> has recently made a comprehensive survey of melting-point data for metal oxides and discusses some of the problems involved. He notes that the melting points of the metal oxides are one of the most studied but least known of the physical properties.

In melting-point determinations, it is important that the modern temperature scale be used. Its importance has been discussed by Schneider<sup>13</sup> and Walker.<sup>14</sup> Further status of the measurement of high temperatures is the subject of a 1964 conference,<sup>15</sup> and of a recent book.<sup>16</sup>

### C. Heat-Capacity Data

Turning first to the available low-temperature heat-capacity data, it may be noted that there are many compounds (and even elements) which have not been subjected to low-temperature heat-capacity studies. As might be expected, the elements have been most thoroughly studied. Of the compounds, the oxides have been most thoroughly studied. However, even for the oxides there are many gaps, and often they have been the subject of only a single investigation. For the other compounds; i. e., the borides, carbides, and nitrides, there are even less data. For all of these groups,

there have been very few investigations which have measured heat capacities for a range of compositions in a single metal-nonmetal system.

In addition to the need for further low-temperature data, there is a need for interpretation of the data and comparison with equilibrium measurements to ascertain the entropy at absolute zero.

The term high-temperature heat-capacity measurements refers to data obtained above 298.15°K. Until relatively recently, most high-temperature data for solids have been restricted to the range from 298.15° to 2000°K. However, this range has now been extended upward to the vicinity of 3000°K in some cases.

In general, it appears that the accuracy of the very-high-temperature data is not very good. Clearly, there is a need for much further work in this area. Furthermore, the problems of measuring heats of transition and heats of fusion must be given greater emphasis. Particularly lacking are experimental evaluations of the heats of fusion.

Heat capacities and knowledge of liquids at high temperatures are practically nonexistent. Here, there is a need for both experiment and theory.

#### D. Heats of Formation

In determining the heat of formation of a compound, it is often tempting to accept the calorimetric determinations in preference to others. However, equilibria data (if carefully executed) can provide precise values. It is, therefore, desirable to achieve heats of formation by as many independent ways as possible.

In the present work, there have been many occasions where heat-of-formation values have not been available. Thus for the borides, only a limited amount of data has been obtained. Generally, this has been limited to the refractory diborides. The others are virtually untouched. The data for the oxides are the most complete, but even there, still many compounds are in need of further work. Thus, Huber and Holley<sup>17</sup> recently surveyed the status of heat-of-combustion data for the metals. For the carbides and nitrides, there is also a need for further work. Additional heat-of-formation studies for some of these groups of compounds, as a function of composition, are desirable.

#### E. Spectroscopic Constants

For many of the diatomic and polyatomic gaseous species of interest, the required spectroscopic constants are lacking. In the case of the transition metal-monoxide gases, there is often incomplete knowledge of the electronic energy levels. For the gaseous dioxides, there is even less

information available. Hence, it is desirable that these species be studied in greater detail to provide the basic spectroscopic constants necessary to calculate accurate thermodynamic functions.

#### F. Brief Summary of Types of Data Needed

The preceding discussions have shown that in a variety of fields, the data necessary for such works as the present one, are missing. To illustrate briefly this lack, table 88 has been prepared. This table summarizes some of the scientific fields needing further investigation.

**TABLE 88**

**SOME SUBJECTS NEEDING FURTHER EXPERIMENTAL  
OR THEORETICAL INVESTIGATION**

Subject	Type of Data Needed
Phase data	<ul style="list-style-type: none"> <li>(1) Knowledge of compounds formed</li> <li>(2) Homogeneity ranges</li> <li>(3) Melting points</li> <li>(4) Transition points</li> <li>(5) Detailed data which permits the construction of accurate phase diagrams</li> </ul>
Heat capacity data	<ul style="list-style-type: none"> <li>(1) Low temperature data</li> <li>(2) High temperature data</li> <li>(3) Heats of transition</li> <li>(4) Heats of fusion</li> </ul>
Heats of formation	<ul style="list-style-type: none"> <li>(1) Calorimetric data</li> <li>(2) Equilibrium data</li> <li>(3) Theoretical estimates</li> </ul>
Spectroscopic constants	<ul style="list-style-type: none"> <li>(1) Energy levels for rare earths and actinides</li> <li>(2) Data for diatomic species</li> <li>(3) Data for polyatomic species</li> </ul>

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